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Black willow (Salix nigra) use in phytoremediation techniques to remove the herbicide bentazon from shallow groundwater

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BLACK WILLOW (*SALIX NIGRA*) USE IN PHYTOREMEDIATION TECHNIQUES TO REMOVE THE HERBICIDE BENTAZON FROM SHALLOW GROUNDWATER

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DEDICATION

I dedicate this dissertation to my family. My father, R. F. "Blondie" Conger, who taught me the importance of hard work and instilled in me the perseverance and strength to overcome all hardships. My mother, Martha Conger, who gave me love, cared for me and encouraged me to pursue my education. My wife, Laurina Amos Conger and children, Matthew, Meredith, Maxwell, and Michael Conger, who have given me love and support over the past eight years.

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ABSTRACT

Wetland environments have been impacted by the activities of man over the past several hundred years in North America. Industrialization into wetland areas has brought with it anthropogenic compounds that have been released into soils and groundwater. The use of phytoremediation to detoxify soil and groundwater began in the mid 1990's and has become a popular remediation technology. In 1994, a feasibility study for using phytoremediation in such an industrialized wetland area was conducted at a petrochemical facility at BASF Corporation, located about 20 kilometers south of Baton Rouge, Louisiana in Ascension Parish. The test site consisted of low level concentrations of the herbicide bentazon in the shallow soil and groundwater. In 1996, two test plots of 438 and 1000 black willow saplings were planted over the two shallow groundwater plumes of bentazon contamination.

Groundwater monitoring, which began five years prior to plantings, was continued for five additional years after plantings. An effectiveness study was concluded in 2001. This research included measuring plant water use, soil conditions, evapotranspiration rates. Groundwater and statistical modeling were used to evaluate phytoremediation effectiveness. Data support that phytoremediation at the test site was successful at reducing the concentration of bentazon from the shallow groundwater. Modeling studies demonstrated that effective remediation will continue to occur as the trees continue to grow. It is predicted that remediation will be completed within 22 years. This research demonstrates the first comprehensive phytoremediation approach to remove the herbicide bentazon from shallow groundwater.

CHAPTER 1: PHYTOREMEDIATION AS AN APPROACH TO ANTHROPOGENIC CONTAMINATION IN INDUSTRIALIZED WETLAND ENVIRONMENTS

1.1 Industrialization of Wetland Areas

Industrialization of wetland areas has occurred extensively during the last three-hundred years in North America. Wetland environments including coastal wetlands and inland wetlands have been impacted by the activities of man. In the United States, more than 50% of wetlands have been lost since the early 1700's (Mitsch and Gooselink, 1993). Activities including agricultural development, oil and gas exploration and production, transportation infrastructure, industrial manufacturing, timber harvesting, and real estate development have impacted these environments through changes that have resulted in a net loss of wetland environment. Wetlands provide valuable benefits including habitat for wildlife, recreation, flood and storm protection, minerals and fisheries. In order to exploit wetland areas, canals have been used to drain wetland areas of water, wetland vegetation has been removed to change the land use, and wetlands have been levied restricting seasonal water inundation and nutrient cycles, all of which have resulted in changing the functional wetland habitat.

With the industrialization of wetland areas has come other environmental damage including the release of toxic pollutants into the land and water. These toxins have not only afflicted man with health threats, but also further diminished the viability of wetland function through the destruction of fauna and flora. Soil and groundwater contaminated with anthropogenic compounds required that regulatory action be taken to remediate and restore the original soil and groundwater chemistry to the effected areas. Environmental remediation requirements resulted in the development of numerous scientific techniques to restore soil and groundwater conditions.

One technique that has been developed to detoxify soil and groundwater is phytoremediation. This chapter introduces the use of phytoremediation for the restoration of soil and groundwater conditions at an industrialized area located in a riparian wetland area in South Louisiana. This project used black willow (*Salix nigra*), a common wetland species in alluvial river swamps (Conner and Day, 1976) to remove the herbicide bentazon from shallow groundwater.

1.2 Environmental Restoration Through Phytoremediation Technology

Phytoremediation is a natural method that uses plants to detoxify organic and inorganic pollutants in groundwater and soil (Bollag et al., 1994). It has also been referred to as rhizosphere technology for the symbiotic relationships that exist between plants, soil microorganisms, and fungi (Walton et al., 1994). The rhizosphere is a zone of interaction between plant roots and soil microorganisms where biochemical processes occur in a communal relationship between both. Plants act on hazardous organic substances by uptake and accumulation, by metabolism, and by microbial transformation (Shimp et al., 1993). With an organic contaminant as a substrate, aerobic biodegradation in the rhizosphere can be explained as follows:

$$CH_mO_1 + aNH_3 + bO_2 \rightarrow y_cCH_pO_nN_q + zCH_rO_sN_t + cH_2O + dCO_2$$

$$\text{Contaminant (Substrate)} \rightarrow \text{Biomass} + \text{Extracellular Product}$$

(Shimp et al., 1993)

Fungi also play a very important, but less understood, role in the rhizosphere. Almost all plants are associated with fungi that may form symbiotic relationships with plant roots. The plant supplies energy-rich organic solutes to the fungi while the fungi provide mineral nutrients to the plant (McFarlane and Traff, 1995). These are referred to as mycorrhizae and have been shown to increase water availability and translocate nutrients from soils to plants. The influence on uptake and chemical metabolism is not well understood.

The uptake and transpiration processes are some of the most important processes in phytoremediation methods. Transpiration serves as the mechanism of transport that enables plants to use mineral nutrients collected at the roots. Water serves as a solvent, a transport medium, and as a reactant for the uptake, translocation, and degradation of anthropogenic chemicals within the plant tissue (McFarlane and Traff, 1995). Since water is so very essential, plants that use large amounts of water, and also sunlight, will be the most appropriate for soil and groundwater remediation by phytoremediation technology.

Such plants, termed phreatophytic vegetation, rely on large supplies of water and consequently have high transpiration capabilities. Phreatophytes are suitable for phytoremediation because of their typically high water usage rates and their fast growth rates (Gatliff, 1994). Although root systems of plants are variable, it is generally true that the size of root systems is often proportional to the visible aboveground portion of the plant (McFarlane and Traff, 1995). However, it must be recognized that roots serve plants as anchorage, as well as nutrient storage and transport for the plants. Some plants may have extensive root systems for that purpose as well. Conversely, some plants may have less extensive root systems because of community relationships among other individuals, but they also may be highly transpiring plants.

Another important feature of phytoremediation techniques is the relationship between root exudates and rhizodeposition. This relationship is important in stimulating aerobic biodegradation of the chemical substrate prior to plant uptake. As a plant grows, root systems expand progressively, and fine roots and root hairs die and decay as the roots grow outward. This process, known at rhizodeposition, allows the decaying root material to act as a substrate for enhanced microbial activity (Shimp et al., 1993). Root exudates are secretions that leak from epidermal or cortical cells of a plant root. These secretions are a result of metabolic activity as a plant consumes nutrients. Exudate composition varies between plants, but can include sugars, amino acids, organic acids, fatty acids, sterols, growth factors, nucleotides, flavanones, enzymes, and numerous other compounds. This process provides additional substrate for microorganisms, which may be essential to degrade soil contaminants.

The rhizosphere can also influence other chemical processes, which may be critical to organic chemical biodegradation. Nitrogen fixation, solubilization of phosphorus, trace mineral transfer, and oxygen transfer all play important roles in the stimulation of microbial activity in the rhizosphere. Nitrogen, which is a limiting factor in plant growth, can be fixed in soils by several processes. The largest and most important of which is symbiotic or nonsymbiotic biological nitrogen fixation (Shimp et al., 1993). The symbiotic relationship between legume plants and heterotrophic bacteria allows nitrogen fixation to occur in plants. Some bacteria, such as *Azotobacter* and *Clostridium* are capable of nonsymbiotic nitrogen fixation, as well. These relationships result in more nitrogen for plant growth and, subsequently, more organic substrate for microbial consumption. This stimulates microbial activity and furthers biodegradation of organic contaminants before uptake into the plant.

According to Shimp et al. (1993), phosphorus uptake from soil is not optimal without the biological activity in the rhizosphere. Some bacteria, such as *Bacillus*, *Pseudomonas* and *Agrobacterium*, improve the uptake of phosphorus by plants (Shimp et al., 1993). The rhizosphere is able to solubilize phosphorus by the chemical activity of the root exudates in association with these bacteria, thereby improving the benefits to plants and to microorganisms in the rhizosphere by continued growth.

Trace mineral transfer from microbes is similar to the nitrogen and phosphorus uptake process by plants. Root exudates and dead root material were once part of a living plant; therefore, they contain trace minerals, which in turn are available to the consuming microorganisms. This process results in a healthier microbial community, which is more capable of biodegrading the organic contaminants in the rhizosphere.

Oxygen transfer is a function of the plant that is most critical to microorganisms, particularly as soil depth increases. At greater depth anaerobic conditions will prevail, limiting the ability of aerobic microorganisms to biodegrade organic wastes. Trees such as bald cypress and black willow are known to transport oxygen into the rhizosphere. Wetland vegetation is commonly more adapted to provide oxygen transfer due to its habitat requirements. Non-wetland vegetation is less able to provide for oxygen transfer into the rhizosphere. The transfer of oxygen into soils in the rhizosphere is important to maintain aerobic conditions and stimulate aerobic microbial activity.

There are several potential phytoremediation mechanisms that can be encountered in part or whole within any application of phytoremediation technology. These include phytoextraction, rhizofiltration, phytostabilization, rhizodegradation, phytodegradation, and phytovolatilization (USEPA, 2000). Table 1.1 illustrates these mechanisms and their applicability to phytoremediation project goals.

Table 1.1: Phytoremediation Mechanisms

Mechanism	Effect	Media	Contaminants	Plant Types
Phytoextraction	Contaminant Extraction and Capture	Soil, sediment, sludge	Metals, Radionuclides	Mustards, sunflowers, poplars
Rhizofiltration	Contaminant Extraction and Capture	Groundwater, surface water	Metals, Radionuclides	Mustards, sunflowers, water hyacinths
Phytostabilization	Contaminant containment	Soil, sediment	Metals	Mustards, poplars, grasses
Rhizodegradation	Contaminant destruction	Soil, sediment, sludges, groundwater	Organic Compounds	Mulberry, grasses, poplar, cattail, rice
Phytodegradation	Contaminant destruction	Soil, sediment, sludges, groundwater, surface water	Organic compounds, chlorinated solvents, phenols, herbicides	Algae, stonewort, poplar, black willow, cypress
Phytovolatilization	Contaminant extraction from media and release to air	Groundwater, soil, sediment, sludge	Chlorinated solvents, some inorganics	Poplar, alfalfa, black locust, mustards

(USEPA, 2001)

Phytoextraction is attributed to the removal of a contaminant by uptake processes into the plant tissue using translocation. When this mechanism is active, the phytoremediation application requires that the contaminant is removed from the environment by harvesting the plant. This mechanism can be more appropriately applied with plants that hyperaccumulate metals (Reeves and Brooks, 1983). These might commonly include phreatophytes such as mustards, sunflowers, tobacco, and poplar trees.

Rhizofiltration and rhizodegradation both use the beneficial symbiotic relationships between soil microbes and plant roots and exudates. Rhizofiltration extracts and captures contaminants, whereas rhizodegradation goes one step further and destroys contaminants in the root systems. Rhizofiltration is more beneficial in applications requiring the removal of metals from groundwater or soil, whereas, rhizodegradation is more beneficial in applications that include organic contaminants. Although it has not been studied in this research, the use of phytoremediaton for treatment of surface water as an ex-situ method is also a valid application for the rhizofiltration and rhizodegradation.

Phytostablization can result in the fixation of mobile or toxic contaminants within the root zone either by immobilization through absorption and accumulation by roots, or precipitation within the soil in the root zone. Phytostabilization will occur through root zone microbes and soil chemistry as associated with the exudates and the production of carbon dioxide. Phytostablization can lower the solubility of metals and their mobility. This mechanism acts to dissociate organic compounds through processes such as hydrolysis and adsorption (USEPA, 2001). This mechanism may enable stabilization of toxic metals and/or organic compounds to levels suitable for long-term monitoring in lieu of removal from the soil.

Phytodegradation results when contaminants are degraded within plants through metabolic processes or through degradation external to the plant through the effects of enzymes produced by the plant. Transformation, uptake and metabolism processes that occur within a particular application account for phytodegration mechanisms. Uptake and transformation are dependent upon the contaminant hydrophobicity, solubility, and polarity. Many researchers have generally assumed that the octanol-water coefficient (K_{ow}) can provide a good indication of the degree of uptake that could be expected for a specific contaminant (Schnoor et al., 1995). Those contaminants found to have log K_{ow} values between 0.5 and 3 are most conducive to uptake in plants, while those with higher values may still be translocated into the plant, but will be less conducive to uptake mechanisms. Contaminants with high water solubilities and low sorption properties will also be more conducive to plant uptake. Hydrophobic compounds typically are found bound to the root surfaces or partitioned, but are not translocated beyond the roots (Schnoor et al., 1995). Nonpolar molecules with molecular weights less than 500 typically are found to adsorb to root surfaces. Conversely, polar molecules will enter the root and be translocated (Bell, 1992). Metabolism can play a significant role in the phytodegradation of contaminants as well. Herbicides such as atrazine are metabolized within the plant (Burken and Schnoor, 1997). Phytodegradation can result in the formation of toxic intermediate chemicals from the original contaminant or result in the creation of less toxic compounds, thus having a beneficial effect. Phytodegradation is a common process in hybrid poplar, black willow, and cypress trees. Another related process that is sometimes found to occur with phytodegradation is phytovolatilization. It depends upon the same processes of metabolism, uptake and translocation that phytodegradation does, except that it results in the release of the metabolites or the contaminant itself into the atmosphere. It can often result in the production of less toxic compounds and can result in additional degradation through photodegradation.

As previously mentioned, a phytoremediation research project with black willow, a wetland specie, was developed to address shallow groundwater contaminated with the herbicide bentazon at an industrialized area of former wetlands in Southern Louisiana. This research project was developed after the discovery of bentazon in the groundwater from the facility operation.

1.3 Bentazon Contamination of Shallow Groundwater at an Industrial Facility

In 1994, a feasibility study was conducted to determine potential remediation alternatives at a location within the BASF Corporation Facility located about 20 kilometers south of Baton Rouge, Louisiana in Ascension Parish (Figure 1.1). BASF Corporation is the North American subsidiary of the German chemical company, Badische Anilin Soda Fabrik (BASF). The facility produces a wide variety of chemicals for the automotive, home construction, cosmetics, and pharmaceutical industries within the United States and abroad. The developed portion of the facility includes about 350 hectares of a total 1000 hectares of contiguous property owned by BASF in Ascension Parish. BASF acquired the facility from the former owner, Wyandotte Chemicals, in the late 1960’s. Development of the property by Wyandotte Chemicals began in the late 1950’s.

The facility has been continuously expanded since the 1950’s. In 1991, siting activities were begun on a portion of the undeveloped lands at the BASF Facility to locate and construct a new facility to biologically treat wastewater from the chemical process units. A 30-hectare plot of land was chosen as a potential site and an assessment of the soil and groundwater was made. Between 1978 and 1982, the chosen site had been formerly used for the dewatering of digested biomass sludge from the facility secondary

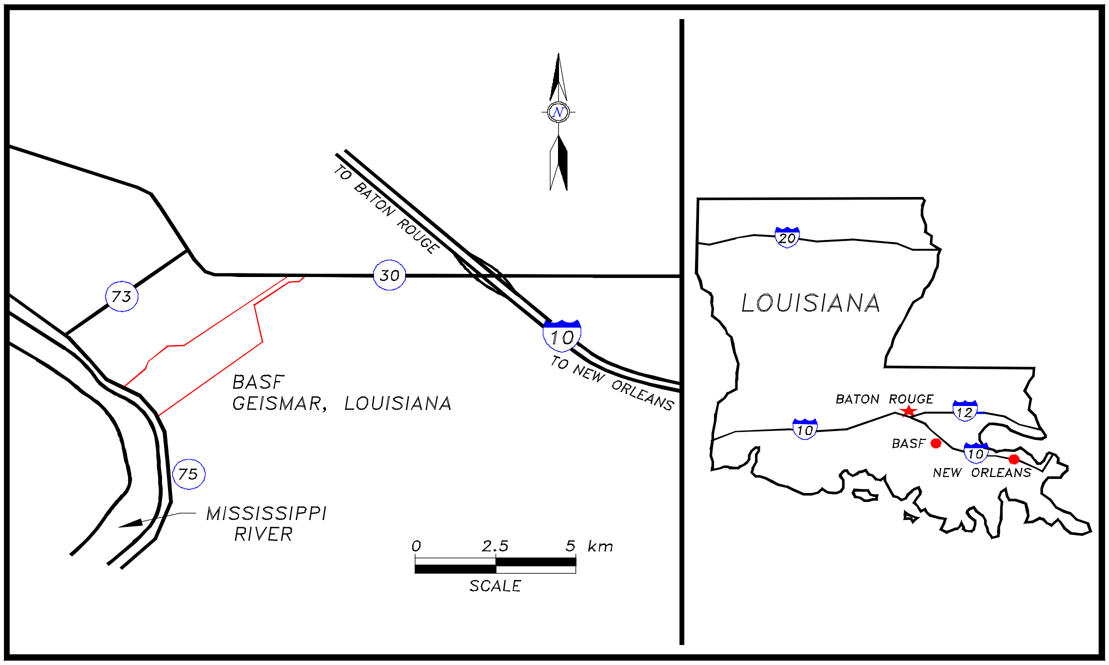


Figure 1.1: Location of the Phytoremediation Test Site at BASF Corporation, Geismar, Louisiana

treatment plant. The sludge had been stored on the site in aboveground surface impoundments, which were used to dewater it. These impoundments were constructed of earthen materials with no liner system to prevent any leakage from the sludge into the shallow soils and groundwater. In 1983, BASF ceased the use of these impoundments and disposed of all the sludge at a commercial landfill. The impoundments were completely removed, and the area was returned to vacant land, until it was considered as a possible location for the new wastewater biological treatment facility in 1990.

It is believed that the study location at BASF was contaminated through the sludge dewatering process with low-level concentrations of the herbicide bentazon (Conger, 1995). The Louisiana Department of Environmental Quality required the remediation of the site according to the directives of the State Environmental Quality Act. Conventional remediation methods using mechanical pump and treat technology would have cost an estimated 1.5 million dollars. Phytoremediation was one of the alternatives studied at this location. The potential economic benefits and the more aesthetic environmental appeal suggested that phytoremediation could be a feasible option for successful remediation (Conger, 1996). The feasibility study included a series of laboratory experiments with six species of phreatophyte trees as potential candidates for phytoremediation plantings. While all the species studied were found to have varying degrees of potential for phytoremediation, the study indicated that the best candidate was the black willow (*Salix nigra*).

In late 1996, black willow was planted at the site as the first large scale phytoremediation project in Louisiana. Two separate areas, of 0.1 and 0.3 hectares, included groundwater plumes of less than 10 mg/l in the shallow groundwater less than one-half meter below the ground surface (Figure 1.2). Black willow trees (*Salix nigra*) were planted in October 1996 at two-meter spacing in both plots, containing 438 trees at Treatment Plot 1 and 1000 at Treatment Plot 2. The remediation plan included the development of studies to document and determine the effectiveness of the method at the BASF location over a five-year period ending in the year 2001. In 1998, after two years of growth, development of a groundwater model was begun to assist in making predictions of the time needed to achieve remediation. First, plant transpiration, a critical factor in deriving water use, was measured through a series of field experiments on each of the treatment plots at the site.

The plant transpiration process is dependent upon several natural factors including available sunlight, soil moisture and nutrients, canopy variation, plant size, and climatological conditions that make it difficult to accurately measure In this study, a non-

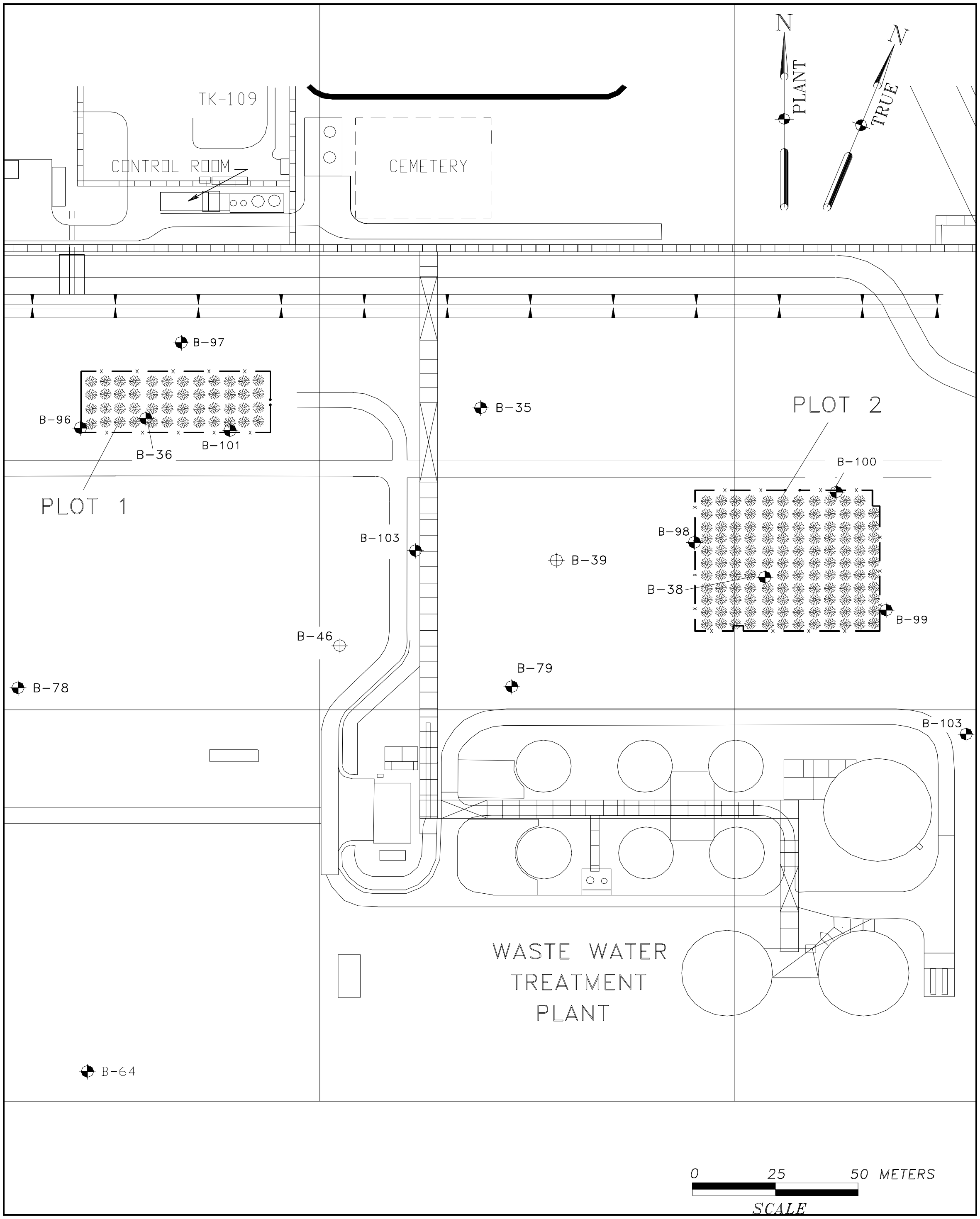


Figure 1.2: The Phytoremediation Test Plot Locations at BASF Corporation

intrusive method of obtaining transpiration rates or sap flow was used to derive the monthly water use for both experimental trial plots during the 1998 and 1999 growing seasons.

The tree-trunk heat balance (THB) method was used in two series of monthly experiments conducted during the growing seasons of 1998 and 1999. This method, developed by Sakuratani (1981) and further refined by Baker and van Bavel (1987), was used exclusively during both series of experiments. The intrusive and destructive method, known as the Thermal Dissipation Method (TDP) (Granier, 1985), was also evaluated with limited success in 1998 and was not pursued in favor of THB method. The THB method is based upon the principles of associating the thermodynamic heating of water between reference points with sap flowing through the conductive tissues of the plant xylem and phloem, collectively referred to as sapwood.

At the conclusion of the studies of transpiration, groundwater modeling was done on the test location. Groundwater modeling techniques were used predict the length of time necessary to achieve successful results. Success, for the purposes of these studies, was set as the point where no negative impact to human health or the environment occurred. Soil sampling was performed to characterize soil physical properties and nutrients.

To evaluate observed groundwater monitoring trends, the use of a time-series statistical method, known as Bayesian statistics, was used (Pole et al., 1994). A Before-After Control-Impact Model (Smith, 2002) of the data was evaluated using analysis of variance methods to determine if significant changes in bentazon concentration could be statistically validated after phytoremediation was begun in October 1996. Prior to phytoremediaton, five years of groundwater monitoring was performed between July 1991 to October 1996 on a semi-annual frequency. Groundwater monitoring data after October 1996 were compiled monthly and compared to the five years of semiannual monitoring. The Bayesian statistical method provided very useful analyses to determine the progress of remediation. The statistical model included the evaluation of other limiting environmental factors that could affect the outcome of the remediation project, which included the river stage, groundwater level, and evapotranspiration rate.

1.4 Phytoremediation Research at BASF Corporation

The 1991 environmental assessment uncovered residues of bentazon at the site (Woodward-Clyde Consultants, 1991). Bentazon had been treated at the secondary treatment plant beginning in 1978, and was present in the resulting sludges. Bentazon production at BASF ceased for economic reasons at Geismar in 1987. The suspected source of this undegraded bentazon was leachate from the sludge stored in the former surface impoundments. The leachate was suspected to have percolated into the shallow soil and groundwater prior to closure of the surface impoundments. Since this sludge had been removed, no source for continuing releases remains at the site. Based on these findings, the regulatory agencies required the relocation of the proposed new wastewater treatment facility until further assessment and possible remediation needs could be evaluated at the bentazon site.

In 1994 a remediation feasibility study was begun. This study found that phytoremediation was a feasible alternative (Conger, 1995). A subsequent laboratory experiment to evaluate phytoremediation of bentazon with six different tree species found that black willow had the most promise for successful remediation (Conger, 1996). This research, performed as the author’s master’s thesis project, included the examination of phreatophytic behavior and the potential ability to mineralize bentazon.

An earlier study determined that bentazon was principally dissolved in the groundwater at the site (Conger, 1995). Little, if any, bentazon was believed to be adsorbed in the soil, as supported by the physical characteristics of bentazon (Ney, 1995). Bentazon is infinitely soluble in water and has a vapor pressure of <0.1 x 10^{-7} mm Hg (20°C), making it highly mobile in groundwater and less volatile under normal temperature and pressure. Research on bentazon fate (Chiron et al., 1995) has found photolysis as a major process in bentazon degradation. Derivative compounds can not be easily identified nor quantified, thus making fate determination by most analytical methods very difficult. Recent laboratory studies on the fate of bentazon in soils have used radiolabeled tracer derivatives and determined that 12-15% of bentazon is mineralized immediately, 5% is methylated and subsequently dimethylated to carbon dioxide, and 65 to 85% is hydroxylated to 8-hydroxy bentazon (Knauber et al., 2000). This 8-hydroxy bentazon is bound to humic matrix or further mineralized to other organic acids. The rate of mineralization by aerobic microbes is very slow, as found in these studies. Bioremediation studies performed for other BASF remediation projects support that bentazon is not easily biodegradable (Woodward-Clyde Consultants, 1992). Anaerobic biodegradation would be expected to be even less possible.

Bentazon is considered moderately toxic and has a log octanol-water coefficient (K_{ow}) of 2.2, thus highly hydrophobic. This suggests a low potential for bioaccumulation in the food chain (Ney, 1995). Phytoremediation research, while limited on many organic compounds, has found in general that organic compounds with log K_{ow} above 3 are less able to be translocated within plants and become bound in the root systems (Schnoor et al., 1995), suggesting bentazon is likely to be translocated by plants.

During a 1995 feasibility study (Conger, 1995), a general review of successful phytoremediation projects was undertaken, which found that the poplar tree had been used in several instances due to its phreatophytic behavior and relatively high tolerance to toxins. The poplar tree and the black willow tree both belong to the *Salicaceae* family of trees. The black willow (*Salix nigra*) is common to South Louisiana and is found along the Mississippi River near the bentazon site. This species was chosen for testing along with the yellow poplar (*Liriodendron tulipifera*), and other indigenous species, including the bald cypress (*Taxodium distichum*), river birch (*Betula nigra*), cherry bark oak (*Quercus falcata*) and live oak (*Quercus virginiana*).

Several assumptions were made prior to designing the lab experiment. First, it was assumed that the agricultural conditions of the soil at the specific bentazon site would be conducive to growing any of the five tree species being tested, since it was previously agricultural land and had been fallow for several years. Before any full-scale implementation could begin at the site, an agronomic assessment of the soils would be performed to provide any necessary chemical adjustments for maintaining conditions that were conducive to tree growth. Obviously, in some cases, this might not be practical.

Second, it was assumed that the soil sorption of bentazon would be negligible due to its chemical and physical properties as a herbicide. Bentazon's physical and chemical properties (Ney, 1995) further support this. As previously mentioned, the K_{ow} effects were assumed to be negligible since bentazon is a herbicide with high mobility. With other contaminants, it could be possible that these constraints would make phytoremediation less successful or completely unsuccessful.

Third, it was assumed that the microbial activity in the rhizosphere could not be adequately duplicated outside the specific site, and since bentazon appears difficult to biodegrade, it would not play an important role in the phytoremediation at the test location. With other contaminants, the microbial activity may be a significant process for successful phytoremediation. However, in this application it is considered to be of minimal effect.

Fourth, the volatility of bentazon was considered unimportant for the purposes of this experiment. This assumption was based on both the physical properties of bentazon and the fact that specific site groundwater monitoring since July 1991 has indicated no decrease in observed bentazon concentrations, suggesting that even though the groundwater is shallow, temperatures are not high enough to result in soil gas vapor loss. In other cases, volatile contaminants might present a more difficult challenge to the experimental design for phytoremediation feasibility tests.

The transpiration evaluations conducted at BASF during the 1995 laboratory research project demonstrated that black willow trees had favorable growth and high water use during the growing season. In addition, the study concluded that black willow trees could tolerate bentazon at the expected field observed concentrations of between 1 to 10 mg/l. Based on the outcome of this study, a full-scale phytoremediation program was begun in October 1996 with the planting of two plots of black willow. This was the starting point for the author's dissertation research.

1.5 Chemical Properties of Bentazon

Bentazon is a heterocyclic nitrogen herbicide developed by BASF in Germany for marketing as a post-emergent broad leaf weed killer for use in soybeans, corn and rice. It has been registered, manufactured and sold in the United States since the late 1970's. As a post-emergent herbicide it effectively destroys the ability of the weeds to photosynthesize (WSSA, 1979). Bentazon is commonly described in research literature in its organic acid form ($C_{10}H_{12}N_2O_3S$), but it is often distributed in its sodium salt form ($C_{10}H_{11}N_2NaO_3S$) in the agricultural market. The properties of both forms are similar, except that the sodium salt form is infinitely soluble in water. It is manufactured by BASF under the registered name Basagran® and is produced in both aqueous and dry formulations. It has a density of 1.21 grams/milliliter, a molecular weight of 240.3, and is a rather stable, non-polar organic salt that is extremely mobile in groundwater. It is not easily sorbed or bound to soil (USEPA, 1988). Herbicides rely on mobility to attack weed plants; therefore, these properties are desirable to that end.

Bentazon is a moderately toxic herbicide with a LD_{50} of 1860 milligrams/kilogram for laboratory rats (BASF, 1992). Even though it is moderately toxic, EPA has established a 0.020 mg/l lifetime health advisory for bentazon in drinking water (USEPA, 1989). Current studies are inadequate to determine if bentazon is a carcinogen or teratogen. Bentazon attacks weed vegetation by disruption of photosynthesis. The concentrations observed at the BASF test location are not expected to be systemically lethal to vegetation. Normal herbicide usage of Basagran® is 1 to 2% per hectare, as compared to the 0.001% maximum concentration that has been observed at the test location. Toxicity testing with black willow demonstrated tolerance at these concentrations according to an earlier feasibility study (Conger, 1996).

The environmental fate of bentazon has been extensively studied by BASF, EPA and other researchers since the early 1970s. Bentazon is not sorbed and is highly mobile in eleven types of Illinois soils (Abernathy and Wax, 1973). Recent laboratory studies on the fate of bentazon in soils have used radiolabeled tracer derivatives and determined that 12-15% of bentazon is mineralized immediately, 5% is methylated and subsequently dimethylated to carbon dioxide, and 65 to 85 % is hydroxylated to 8-hydroxy bentazon. (Knauber et al., 2000). Figure 1.3 is adapted from Knauber et al.(2000) and illustrates a model for the flux of bentazon in soils. Derivative or metabolite compounds of bentazon are typically very difficult to identify by routine laboratory methods, which requires the use of radiolabeled bentazon for accurate studies. Derivatives include 6-hydroxy bentazon, 8-hydroxy bentazon, 2-amino-N-isopropyl-benazmide (AIBA), N-isopropyl-sulfamoylanthranilic acid (NISAA), and anthranilic acid. These compounds are generally less toxic based upon limited toxicological data available. Biodegradation is less likely in anaerobic conditions (van der Pas et al., 1998; Wagner et al., 1996) as would be expected at the test location. Photodegradation of bentazon has been studied; oxidation and hydroxylation are the probable main routes of photodegradation that can occur (Chiron et al., 1995). These processes result in the addition of hydroxyl groups that render the parent molecule less toxic.

1.6 Black Willow (*Salix Nigra*) Morphology and Phytoremediation Use

The willow family (*Salicaceae)* is comprised of softwood trees common throughout most of the southeastern United States. There are about 90 species of willow

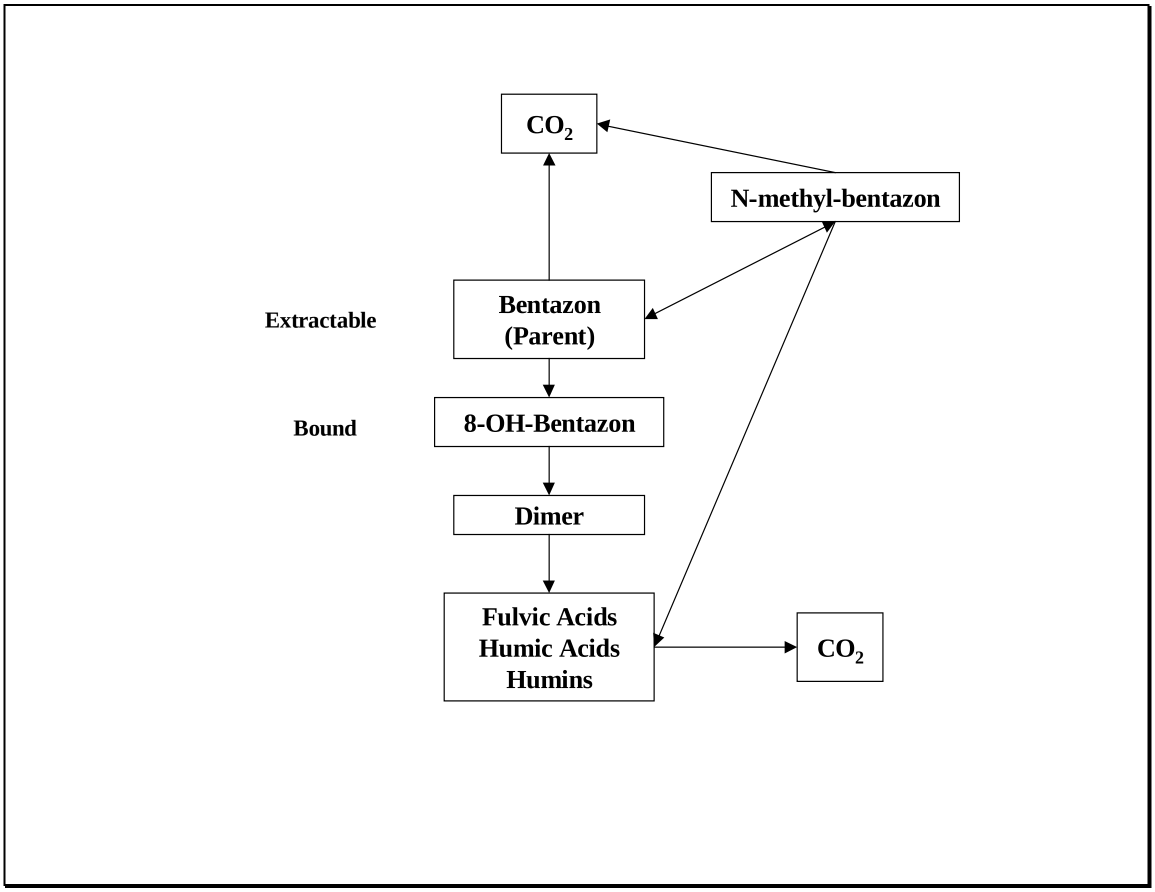


Figure 1.3: Simplified Model of Bentazon Flux in Soils (Knauber et al., 2000)

that are native to North America. Many species may grow to an average height of 12 meters in close stands near water bodies (Photograph 1.1), while heights of 30 meters are not uncommon in some areas. Willows are fast growing deciduous trees with simple leaves (Photograph 1.2). Leaf shapes are serrated to dentate or lobed. Willows commonly have a short life span due to their soft and light wood, and they provide little commercial use as timber or for manufacturing goods. The bark is typically a shaggy bark that appears to be sweet smelling, but bears a bitter astringent taste due to a high content of tannic acid (Duncan and Duncan, 1988).

S*alix nigra*, more commonly known as the black willow, is a member of the willow family and is found as a prolific species across the United States. It is most prevalent in wetland and riparian environments dominated by wet climates and loose soils. It can be found throughout the eastern half of the United States and into the adjacent portions of Mexico and Canada. It grows well in full sun and wet, poorly drained soils. The climate in which black willow grows best is characterized by average rainfall of 1300 mm per year, with an effective growing season from April to August. Average temperatures in suitable climates are 34 degrees Celsius during summer months and 15 degrees Celsius in the winter months, although its distribution is independent of temperature (Sakai and Wiser, 1973).

Photograph 1.1: Black willow trees along the Mississippi River near St. Gabriel, Louisiana

It is typical for black willow to be a succession species in various ecosystems that are subject to natural and man induced environmental changes. Therefore, the species is very common to riverbanks, creek bottoms, lake shores, ponds and freshwater marshes. In general black willow can be found in all ecosytems associated with haplaquent and

Photograph 1.2: Simple Leaves of the Black Willow (*Salix nigra*)

Photograph 1.3: Adventitious Roots on Tree Trunks of Black Willow

In general black willow can be found in all ecosytems associated with haplaquent and fluvaquent soils derived from alluvium. This also lends to it being easily adaptive to water inundation. With its adventitious roots (Photograph 1.3) it can survive long periods of submergence (McKnight, 1965). Black willow will grow in most environments, but having an extensive relatively shallow root system (Photograph 1.4) requires it to have an abundant and continuous moisture supply during the growing season.

Photograph 1.4: Shallow Root System of Black Willow Trees

The black willow reproduction includes no consistently reliable morphological characteristics that can be associated with the identification of the sexes. Male and female are indistinguishable except when flowering. Black willow can flower as early as February and as late as June within its range in North America. Its flowers are yellow to reddish brown and are 25 to 50 mm long cylindrical spikes. The fruit is a catkin of light reddish brown capsules 3 mm long with white tufted seeds. Pollination occurs by insects and release the white tufted seeds for dissemination by wind and water. Seed production is typical after black willows are approximately 10 years old. Seeds, after release, must reach a seed bed within 12 to 24 hours or the viability is greatly reduced. Seedlings can grow as much as 1.2 meters in their first year (McKnight, 1965). Black willow will propagate from fresh seed, root or stem cuttings.

As a phytoremediation plant since 1992, black willow has been documented as having been used in actual remediation projects within the United States at nineteen contaminated locations (USEPA, 2000), not including the BASF site. Each of these documented sites, location, the size, the contaminants of concern, planting dates and media effected are tabulated in Table 1.2. Of these nineteen locations three of them are reported as applications of the phytodegradation mechanism, the process previously mentioned as possibly active at the BASF test location. Unfortunately, only one location reports its results and, due to poor management practices, was not successful. Only one of these documented locations included remediation of herbicides and none included phytoremediation of bentazon. However, twelve of the nineteen are phytoremediation applications for organic contaminants. In summary, while black willow has been used in many phytoremediation applications, its use in remediation of herbicides is minimal.

1.7 Phytoremediation Research Objectives

The BASF test location was planted with black willow (S*alix nigra*) with the intent of using the advantages of phytodegradation and phytovolatilization. The contaminant bentazon, as previously discussed, is a chemical with high water solubility and is very non-polar. While a chemical with a high log K_{ow} of 2.2, studies have previously shown that its metabolites are found in the leaves of the black willow in laboratory studies (Conger, 1996).

Table 1.2: Phytoremediation Projects Using Willow Trees

Location	Size (hectares)	Contaminant	Media	Date Planted
Nevada	2.43	Inorganic	Sand	1997
New Jersey	0.34	Volatile Organics	Soil and groundwater	1996
New Jersey	0.4	Nitrates	Soil and groundwater	1992
Pennsylvania	0.81	Volatile Organics	Fill material	1996
Louisiana	0..2	Volatile Organics	Soil and groundwater	1995
Alaska	Unknown	Pesticides and herbicides	Soil and groundwater	Unknown
Ohio	12.5	Volatile Organics	Leachate and soil	1998
Missouri	0.6	Inorganics, dinitrotoluene	Soils, surface water, groundwater	1996
New Jersey	0.04	Chlorinated solvents	Soil and groundwater	1998
Wisconsin	0.81	Volatile organics	Fill material	1996
Ohio	0.2	Chlorinated solvents	Soil and groundwater	1998
Missouri	0.6	Unknown	Soil	1997
Alaska	Unknown	Volatile organics	Soil	Unknown
Unknown	Unknown	Unknown	Groundwater	Unknown
Louisiana	Unknown	Inorganic	Sludge	1992
New York	Unknown	Leachate	Soil and groundwater	Unknown
New Jersey	3.6	Nitrates	Soil	1992
Ohio	0.2	Volatile organics	Soil	1995
Washington	3.24	Formaldehyde	Groundwater	Unknown

(USEPA, 2001)

It is postulated that bentazon is translocated through plant uptake into the leaves of the black willow. Bentazon is well understood to photodegrade in the presence of light; therefore, it is further postulated that the probable mechanism is photodegradation to its metabolite compounds, which are less toxic, and this is followed by phytovolatilization into the atmosphere that occurs with photosynthesis through the leave stomata. These theories go beyond the scope of this research, however, it is important to postulate the potential mechanisms at work in this phytoremediation application.

There were several research objectives, which were intended to provide not only one of the first case histories of a complete phytoremediation study within an industrialized area of a riparian wetland, but to develop a practical and scientific approach to apply phytoremediation using black willow to a herbicide in shallow groundwater. As previously stated, there are less than twenty documented phytroremediation studies that have utilized willow species (USEPA, 2001). Of those, only one was noted to address a herbicide contaminant in shallow groundwater. Furthermore, only one other was located in an area with as long a growing season as the test location evaluated in this study. Thus, this study should also provide a case history insight into the use of black willow phytoremediation within an area where it was best suited for growth. It would also be unique in the fact that black willow, a wetland specie, would be used in a riparian wetland that has been impacted by heavy industry.

The phytoremediation study objectives were three-fold: (1) estimate the water use of a black willow phytoremediation plot; (2) predict the probable length of time needed to adequately phytoremediate the site; and, (3) evaluate the effectiveness of the phytoremediation plots for reducing the contaminant in shallow groundwater. In this type of environmental restoration, the black willow tree acts as a pumping well to remove the groundwater and contaminant solute contained within it (Gatliff, 1994). Therefore, the objective of being able to accurately measure the water used by the black willow is valuable for long-term planning and to insure that contaminant migration does not occur. This information, used with groundwater modeling techniques, would allow an acceptable scientific prediction of the length of time needed to phytoremediate the test site. Using field data collected through groundwater and soil sampling, the groundwater flow and solute transport mechanisms were evaluated and a time prediction made. To achieve the last objective, to determine the effectiveness of black willow at reducing bentazon concentrations in the groundwater, a statistical model would be developed. It is the goal of this research to establish a practical and scientifically accepted approach to evaluation of phytoremediation with black willow trees a riparian wetland impacted by industrialization.

CHAPTER 2: PHYTOREMEDIATION RESEARCH METHODS

2.1 Research Methods Used for Phytoremediation

This chapter provides the technical references and scientific methods that were used during this research project. A discussion of groundwater sampling and analysis, soil sampling and analysis, meteorology measurements, transpiration and growth rate measurements, groundwater and statistical modeling of bentazon concentrations are presented. Chapter 4 includes the results and discussion and Chapter 5 includes a summary of the findings and conclusions of the research.

2.2 Groundwater Sampling and Analysis for the Herbicide Bentazon

A groundwater sampling and analysis plan was developed prior to phytoremediation during the site assessment phases in early 1992. Additional development of the monitoring system occurred in 1996 to utilize the Before After Control Impact (BACI) Model which will be explained a later section of this chapter (Smith, 2002). Using the BACI Model, the monitoring well program included 4 control set wells, 2 before-after impact set wells and 6 after-impact wells. Well sampling was at a semi-annual frequency from January 1992 to June 1996. After phytoremediation began in October 1996, each plot had one before-after well and three after-impact wells that were monitored monthly through March 2001. Assessment well locations were chosen by stratified random sampling, and phytoremediation monitoring wells were located by equidistant spacing on three sides of the each test plot.

Well installation was by the wet rotary drilling technique according to the required environmental practices of the Louisiana Department of Environmental Quality (LDEQ, 1993). Wells were constructed of Schedule 40 polyvinyl chloride (PVC) pipe.

Well materials and drilling equipment were steam-cleaned prior to installation to prevent contamination. Each well was screened with No. 20 slotted PVC well screens. Assessment wells were constructed of 4-inch diameter pipe, while test plot phytoremediation wells were constructed of 2-inch diameter pipe. The annular space between borehole and the well screen was packed with a sand filter media of coarse silica sand from the bottom of the boring to within 3/4-meter above the well screen. Each sand pack completion was sealed from surface with a 3/4-meter bentonite clay pellet well seal to prevent sample bias from ground surface seepage or upper soil zones into the well screen. All wells were grouted by pumping through a tremie pipe within the annular space from the above the well seal to ground surface. Each well surface completion included a 1.5 by 1.5-meter by 15 centimeter thick concrete pad with an oversized, lockable protective surface casing. Steel posts were placed at the corners of the pads to protect the well from vehicular damage. Each well was outfitted with a gas-driven, dedicated bladder pump to prevent any cross-contamination. Wells were developed using inert nitrogen lift until they produced relatively sediment free groundwater. Conductivity and pH measurements were made on produced groundwater after completion of well development and compared again 24 hours later to determine if well development was adequate.

A standard sampling protocol was used to prevent the bias of samples from cross-contamination. All well sampling was conducted using dedicated bladder pumps driven by nitrogen gas. Wells were purged of stagnant water prior to sampling to avoid bias of water samples. Well water level measurements were taken from each well prior to each sampling for use in groundwater potentiometric surface mapping. Well purging was based on 3 well volumes of pumping and stabilization by measuring pH, conductivity and temperature at each well volume. A portable meter for field testing of pH, conductivity, and temperature was used to make these measurements. This meter was field calibrated to buffer solutions to ensure accurate results. Wells were considered purged once the measured value of these parameters was observed to be within 10% of the prior measurement taken from the previous well volume of purged water.

Well samples were collected in new bottles and cooled to 4 degrees Celsius immediately afterward. Samples were analyzed for bentazon using a liquid-liquid extraction followed by mass spectrometry as prescribed by Standard Method 6640B (APHA, 1998). An analytical detection limit was achieved of 1 ug/l in most instances. Method blanks and field blanks were collected and analyzed to assure quality of all sample analyses. A chain of custody was used to track sample possession and assure quality.

2.3 Soil Sampling and Analysis of the Phytoremediation Test Plots

Soil samples were collected for several purposes during the study and by several sampling techniques. Soil samples were collected during the borehole drilling for monitor well installation to determine the soil texture and geology by the American Society for Testing and Materials (ASTM) method D-2488 (ASTM, 1994). Classifications were made visually by a professional geologist using a soil texture chart of grain size for organic soils. Borehole drill logs of the soil texture were prepared to characterize the subsurface geology.

Soil samples were collected using the split barrel sampler and the thin wall tube sampler techniques according to ASTM methods D-1586 and D-1587 (ASTM, 1994).

The split barrel sampler was used in non-cohesive soils such as sands and advanced by the dropping of a 64-kg steel hammer onto the drill string. The drill pipe was removed from the borehole and the split barrel sampler, equipped with a sediment trap, was disassembled and the sample retrieved. The sampler size was approximately 3.5 cm diameter and 76 cm in length. The thin wall tube sampler was used in cohesive soils such as clays and advanced using the hydraulic power of the mast from the drill rig to push the drill string with the sampler on the end into the soil. The drill pipe was removed and the sample extruded into a sample tray using a hydraulic piston. The sampler size was 7.5 cm diameter and 92 cm long.

Soil samples were also collected for chemical analysis of nutrients and for total organic carbon. These sample locations were selected randomly at each test plot using a random number generator. Each sample was taken using a hand auger with an orchard-barrel sampler according to ASTM method D-1452 (ASTM, 1994). The hand auger was advanced into the soil approximately 20 cm. The sample collected was approximately 8 cm in diameter by 20 cm in length. Samples were collected as individual split cores for analysis of total organic carbon, pH, phosphorus, sodium, potassium, magnesium, calcium, and carbonates. Metals were analyzed by the inductively coupled plasma (ICP) method were used for these analyses (APHA,1998). Table 2.1 provides the analytical methods used for these and other parameters.

2.4 Meteorological Equipment and Measurements at Phytoremediation Plots

Meteorological conditions were measured during the 1998 and 1999 growing seasons at the test plots using a portable tripod mounted weather station. The tripod placed the station approximately 3 meters above ground surface. The equipment was sealed in a weather resistant enclosure to prevent damage and included a ground wire to prevent lightning strike damage. The weather station used in this research was a Dynamet manufactured by Dynamax, Inc. The station was powered by a 10-watt solar panel equipped with a 12-volt battery to allow for 24-hour, hourly measurements of rainfall, surface and soil temperature, solar radiation, relative humidity, wind speed, and wind direction. Data were collected with a Campbell Scientific Model CR10X computer data-

Table 2.1: Analytical Methods Used for Soil Chemical Analyses of Phytoremediation Plots

Analytes	Analytical Method
Total Organic Carbon (TOC)	5220
pH	4500-H^+
Phosphorus (extractable)	3120
Sodium[1]	3120
Potassium[1]	3120
Magnesium[1]	3120
Calcium[1]	3120
Sulfur[2]	3120
Copper[2]	3120
Iron[2]	3120
Manganese[2]	3120
Zinc[2]	3120

(American Public Health Association,1998)
[1]Exchangeable Total Metal
[2]Total Metals as micronutrients

logger and downloaded weekly to a portable computer. Software applications allowed evapotranspiraton to be calculated by the Penman (1948) method.

The instruments included in this weather station are factory calibrated. The rain gauge was a magnetic switch tip accurate to 0.25 mm. The relative humidity sensor was a polymer film surface with a 0 to 100 % range accurate to within 2 %. The anemometer was a cup type with an operational range of 0 to 50 m/s with a gust survival of 60 m/s. It was accurate to ±1 m/s. The wind vane was fitted with a 10K potentiometer capable of an accuracy of ± 5 degrees. The solar radiation detector was a silicon photocell with a typical accuracy of 80 $\mu A/kW/m^2$. The temperature sensor was accurate to ±0.2 degrees Celsius. All recorded data was downloaded from the datalogger weekly to a portable computer and analyzed with standard graphics software.

2.5 Black Willow Transpiration and Growth Rate Measurements at Test Plots

To estimate the water use of the black willow tree plots, a suitable field technique to measure the water use from a group of randomly selected individual trees had to be identified. This water use would represent the degree of phytoremediation occurring through time. Water use can be affected by the meteorological conditions, the rate of evapotranspiration, tree size, growth rate and the degree of toxicity of the contaminated groundwater to the black willow tissue. In summer 1998, field experiments were begun testing the tree-trunk heat balance (THB) method (Sakuratani, 1981; Baker and van Bavel, 1987) and the thermal dissipation probe (TDP) method (Granier, 1985). Both of these methods provided an estimation of sap flow using the same theory, but use differing techniques. The THB method was a non-destructive measurement, while the TDP method required the drilling of holes into the tree, which can lead to damage from water or insects. Studies have shown that both methods can achieve an accuracy of 10% in measuring transpiration rates (Tournbize and Boistard, 1998). The basic difference between the two methods is that the THB method is more applicable to small diameter trees, while the TDP method is more suited to large diameter trees. After field evaluation during the 1998 growing season, the THB was chosen as the more desirable method for measuring sap flow at the test site. This choice was made principally based on the ease of operation and the fact that most trees were smaller diameter than the TDP method would allow.

Field experiments began during the 1998 growing season with a series of 8 experiments of 10 days each on both plots. This was followed by another series of 10 experiments of 10 days each on both plots, performed during the 1999 growing season. Data were collected continuously over 24-hour periods, after which the cumulative sap flow was totaled and a daily mean calculated for each tested tree. These means were subsequently used to develop an estimate of the water use for the tree plot over the entire month.

Growth rates of the trees were measured using two field methods. The first method utilized was the dendrometer technique, which utilizes a strain gauge sensitive to $1/100^{th}$ of a centimeter (Dynamax, 1996). These dendrometers were placed on randomly selected trees during the same time periods that sap flow measurements were made. These measurements were made in 1998. They were discontinued in 1999 for a simple, but laborious approach. This approach was to measure each individual tree at the basal stem once per month. All trees in each test plot were measured monthly using a forester's tree caliper enumerated in millimeters. This field method was performed in both 1998 and 1999 and a single series of measurements was made in 2000.

Test Plots 1 and 2 consisted of 438 and 1000 black willow trees, respectively, planted on 2-meter spacing (Figure 2.1). Experimental series in both 1998 and 1999 included measurement periods of at least 84 hours, which was necessary to obtain accurate results (Devitt et al., 1993). Experiments were performed at each of the two plots each month to obtain monthly measurements of sap flow and allow monthly calculation of water use. Monthly measurements of sap flow were made from June through September in 1998 and from April through September in 1999. The basal tree-trunk diameter was also measured during the same test periods with mechanical calipers to calculate the total available stem area available for water transport. Sap flow tests were conducted as random, stratified sampling events in each respective plot. Meteorological data were collected to determine evapotranspiration (Penman, 1948).

The sap flow experimental apparatus allowed sampling of as many as 16 individual trees during a single test period. Both tree-trunk heat balance parameters, as well as the meteorological conditions, were sampled continuously every 10 seconds and averaged hourly. These readings were collected with the use of an automated field datalogger. A Campbell Scientific CR10X datalogger was used. Data from the logger were downloaded to a portable computer at the completion of an experiment for compilation and analysis.

The tree-trunk heat balance method provides a measurement of the temperature differential of sap that has been heated slightly by the experimental apparatus, as it flows up the xylem toward the tree canopy and passes through a thermopile coil (Figure 2.2).

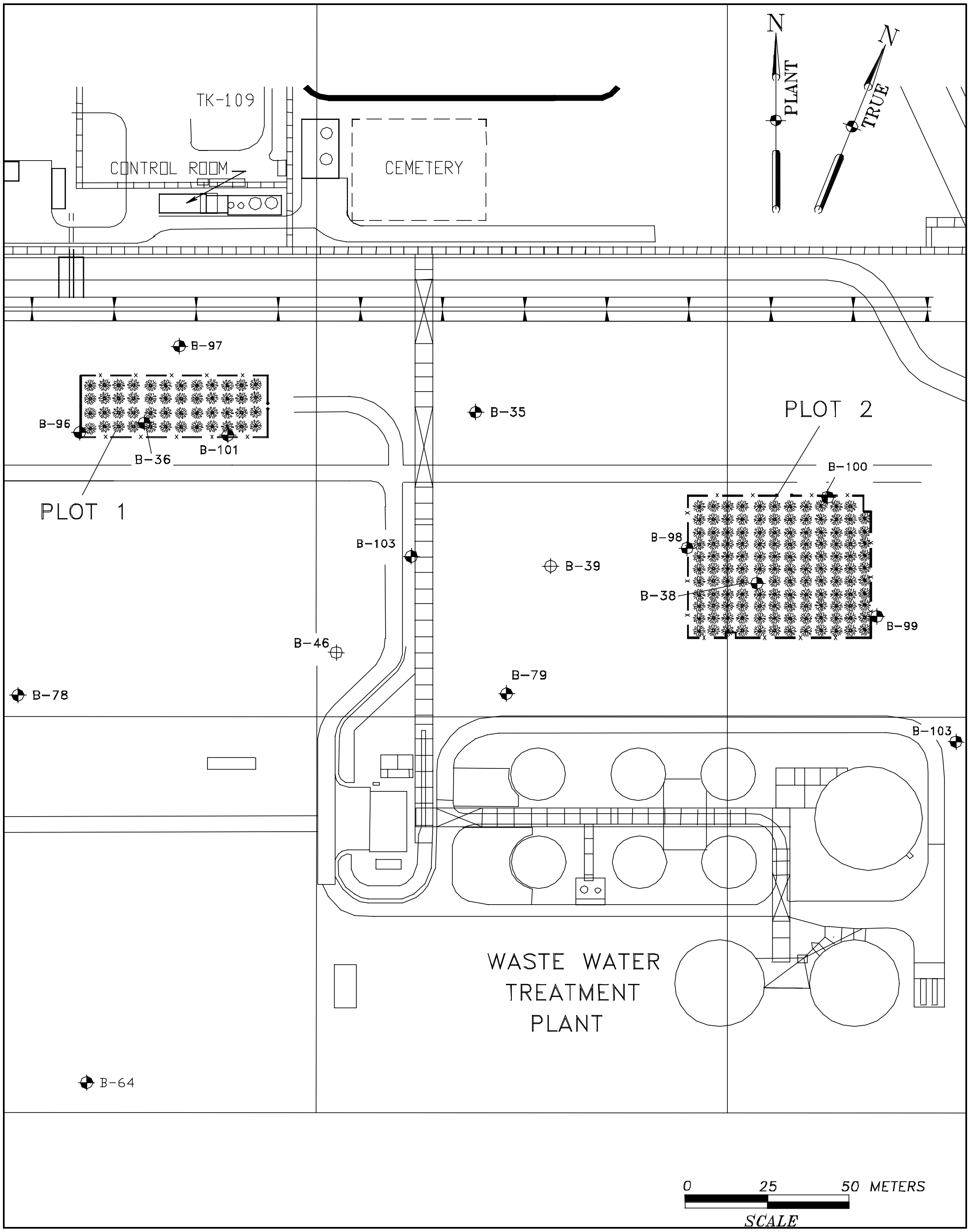


Figure 2.1: Location Map of the Phytoremediation Plots at Test Site at BASF Corporation in Geismar, Louisiana.

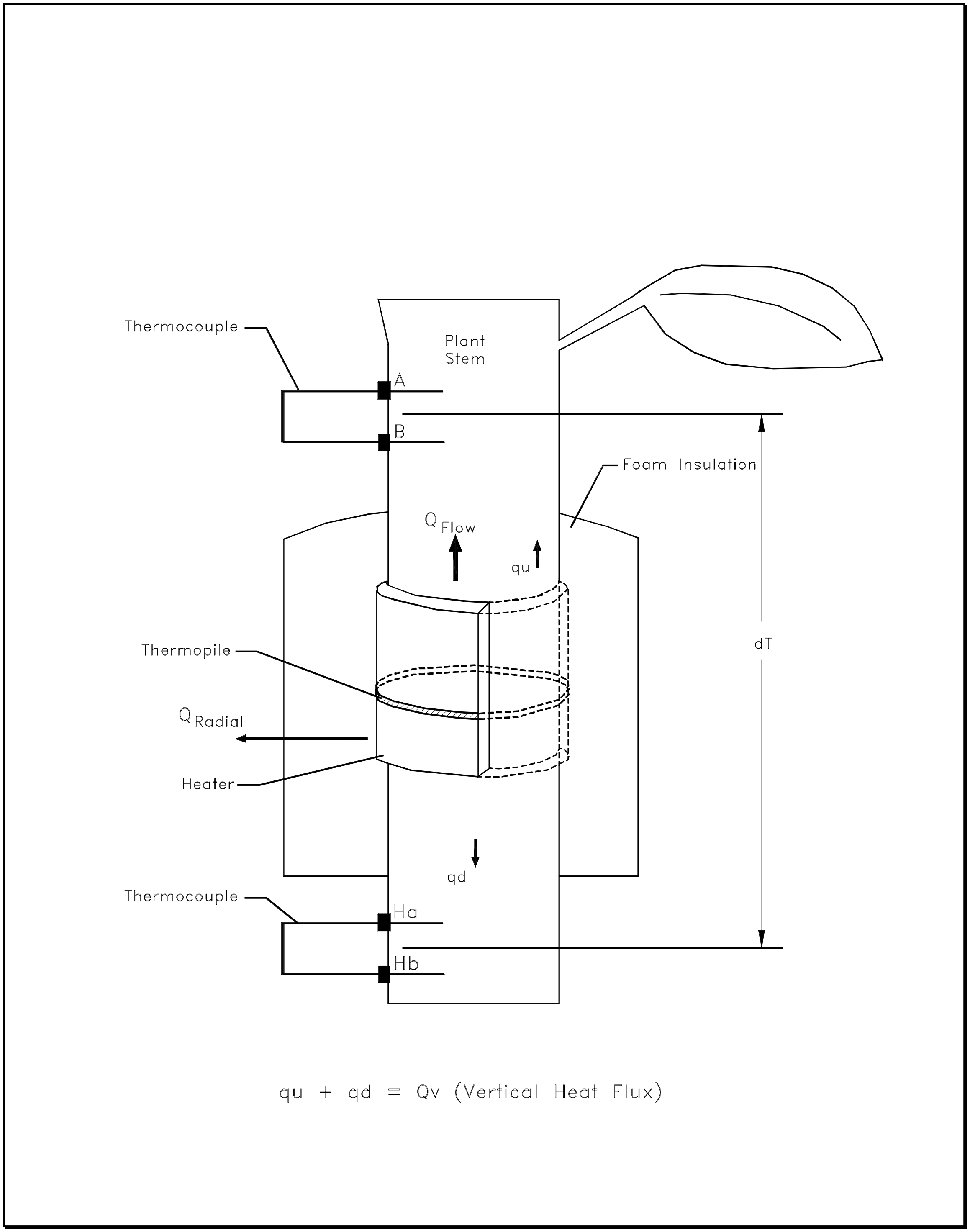


Figure 2.2: Experimental Apparatus and Theoretical Components of the Tree-Trunk Heat Balance Method Used at the Phytoremediation Test Plots at BASF Corporation in Geismar, Louisiana.

The thermopile contains reference points that are positioned at known distances along the tree trunk of known diameter. This measurement leads to the quantification of the sap flow rate. The apparatus utilized to acquire this information is commonly referred to as a stem gauge (Dynamax, 1990). In this series of experiments, it was assumed that the tree trunk or stem being sampled was completely conductive sapwood and has no heartwood. This assumption was made on the basis of the relative size and age of the experimental trees. The calculation basis for sap flow as used in these experiments is:

$$\mathbf{F = (P_{in} - Q_v - Q_r) / Cp{*}dT}$$

(Dynamax, 1990)

Where:

F = Flow rate (g/h)

P_{in} = Power input

Q_v = vertical heat flux

Q_r = radial heat flux

Cp = heat capacity of water

dT = temperature increase in sap

The tree-trunk heat balance method was developed as a non-destructive method to prevent damage to young, small diameter trees (Sakuratani, 1981). Stem gauges of 13, 16, and 19-mm in diameter were used in the experiments conducted in summer of 1998 and 1999. The stem gauges were purchased commercially from Dynamax, Inc., an agricultural testing supply firm. After selecting the tree sample subjects by random number generation, each tree was carefully screened for general suitability to the experimental test based on size, geometry, and health. If a tree, selected by random number generation was determined unsuitable, then the tree nearest to that location was utilized as a proxy.

The sampling point was prepared by gently sanding the corky bark away from the tree trunk with extra fine, 200-grit sandpaper. Non-conductive insulating grease was used to lubricate the tree trunk area and the thermocouple heater. The stem gauge construction consisted of a small electronic circuit board containing the thermopiles and heater, which were encapsulated in weather-resistant mylar plastic. Each gauge was sampled on an individual channel, or cable, connected to the datalogger. Cable plug connections were sealed on the exterior with a wrap of Parafilm™ to reduce electrical shorting related to excess ground moisture. Each stem gauge was tightly secured by urethane foam rubber insulation to contain heat and to prevent airflow interference. Adhesive putty was applied to the topmost foam insulation to prevent electrical shorting attributed to excess moisture. This excess moisture, from precipitation and irrigation, unless sealed out, contributed to the growth of adventitious roots, thus hindering the proper performance of the stem gauge apparatus. A wrapping of Parafilm™ was applied over the foam rubber to further protect the stem gauge. In addition, a reflective heat shield was placed over the Parafilm™ and foam rubber to reduce radiant heat interference. The entire installation was wrapped with aluminum foil to protect the gauge measurements from radiant heat interference.

After all stem gauges were installed and cabled, the data logger was programmed and the computer collection program downloaded. Two dataloggers were used to collect data. Each logger had the capability of logging 8 sample locations, making 16 measurements possible. A 12-volt direct current battery powered each logger, and each battery was attached to a solar panel for daily charging.

The sheath conductivity (Ksh) is a critical variable used to baseline the heat flux. It represents the relationship of the radial heat flux (Qr) to the thermopile output and must be adjusted when zero flow conditions are expected (Dynamax, 1990). This variable is unique to every stem gauge and its relationship to any diameter; therefore, a default value was used initially for the first full daylight period. Once the first zero flow period was experienced at the start of an experiment, the Ksh values were collected from the datalogger for each individual stem gauge and averaged over a three-hour period from 3 am to 6 am. This period was considered a no flow period at the location and time of the experiments described. These averages were then re-entered into the data program, the program was downloaded again, and routine sampling continued. Occasionally, additional Ksh adjustments were made to further improve collected data. The relationship of Ksh to sap flow can affect the resulting sap flow measurement. Therefore, it is important to accurately measure and correct for this variable as needed. At the close of the experiment, raw data were collected from the data logger and transferred to standard computer software allowing statistical analysis and graphing.

2.6 Modeling of Bentazon Transport and Fate in Groundwater

The field data collected from groundwater sampling, soil nutrients, and sap flow measurements were used to model the groundwater flow and solute transport of bentazon in 2001. These groundwater models were intended to provide relative predictions to the length of time needed to phytoremediate the shallow groundwater of bentazon and to predict whether phytoremediation would prevent migration of the contaminant plume away from the test site. The U.S. Geological Survey groundwater model, MODFLOW

(McDonald and Harbaugh, 1988), and the U.S. Environmental Protection Agency transport model, MT3D (Zheng, 1990), were utilized to make these determinations.

As previously mentioned, to accurately model the groundwater, the plant transpiration obtained in the sap flow measurement experiments was used. In combination with projected growth rates, incremental changes on an annual basis in the transpiration rate were made until the trees were assumed to be mature. Maturity was assumed to be 20 meters based on the measured height of other black willows growing in the vicinity. However, at Plot 1, the maturity was assumed to be 10.5 meters, since trees at that location are controlled to that height to protect overhead powerlines.

Calibration steps were necessary to both steady state and transient flow conditions to be able to accurately model the solute transport in future predictions. MODFLOW enables the modeling of the hydraulic phenomena, and when used with MT3D, a simulation of the advection, dispersion and chemical reactions associated with transport can be made. This provides the predictions for concentration and groundwater flow through future time steps. In order to use these models, the necessary flow and transport variables had to be collected for calibration of the steady state model. Table 2.2 includes the model assumptions used for calibration. These assumptions were made from estimates based on actual soil sampling and hydrologic test data. After several reiterations of calibration trial and error, a final calibration was completed to compare the actual potentiometric surface map to the modeled potentiometric surface map. The initial time at calibration was chosen as January 1997, which was about two months before the start of the first growing season at the phytoremediation plots.

Table 2.2: Phytoremediation Groundwater Modeling Assumptions Used at the BASF Corporation Test Location, Geismar, Louisiana.

Model Variable	Assumption Used
Bentazon Decay Rate (mg/l/year)	4.5×10^{-4} (a)
Moisture Content of Zone (%)	26.93 ± 4.48
Effective Soil Porosity (%)	36.3 ± 2.3
Organic Matter Content (%)	1.3355 ± 0.760398
Hydraulic Conductivity (cm/sec)	$4.71 \times 10^{-4} \pm 4.57 \times 10^{-4}$
Black Willow Transpiration Rate (liters/day/m^2)	11.97 ± 0.4285 (b)
Initial Potentiometric Surface	January 1997 Map
Initial Bentazon Concentration Level	January 1997 Map

Notes:
(a) Calculated from the actual analytical data of Well B-36 from October 1996 to March 2001, r^2=0.5305.
(b) Calculated from water use experiments of 1999.

2.7 Statistical Modeling of Bentazon Concentrations in Groundwater

Changes in bentazon concentration in groundwater samples were used as the indicator of phytoremediation effectiveness. A Before After Control Impact (BACI) model was used to arrange data sets and test hypotheses. Figure 2.3 illustrates the basic components of the BACI concept used in this research. To assert that the phytoremediation was effective at reducing bentazon concentrations in groundwater required that evidence supporting a decrease in the concentration after phytoremediation be substantiated and that some other related environmental factor other than the phytoremediation water use could not account for any observed decrease in the bentazon groundwater concentration. Thus, there were two principle hypotheses to test in order to evaluate the effectiveness of phytoremediation. If these hypothesis were to be proven, it would require that the before phytoremediation data indicate no significant decrease and the after-impact data would indicate a significant decrease. The control set would have to indicate that no significant change had occurred in areas outside the influence of phytoremediation.

The usual method of testing BACI designs is to use an analysis of variance approach to evaluate the means of sample data. This test design was further complicated by the fact that all the data were time series and at variable frequencies. Therefore, as an additional tool, Bayesian statistical methods were used to evaluate time series effects not easily visible when using an analysis of variance.

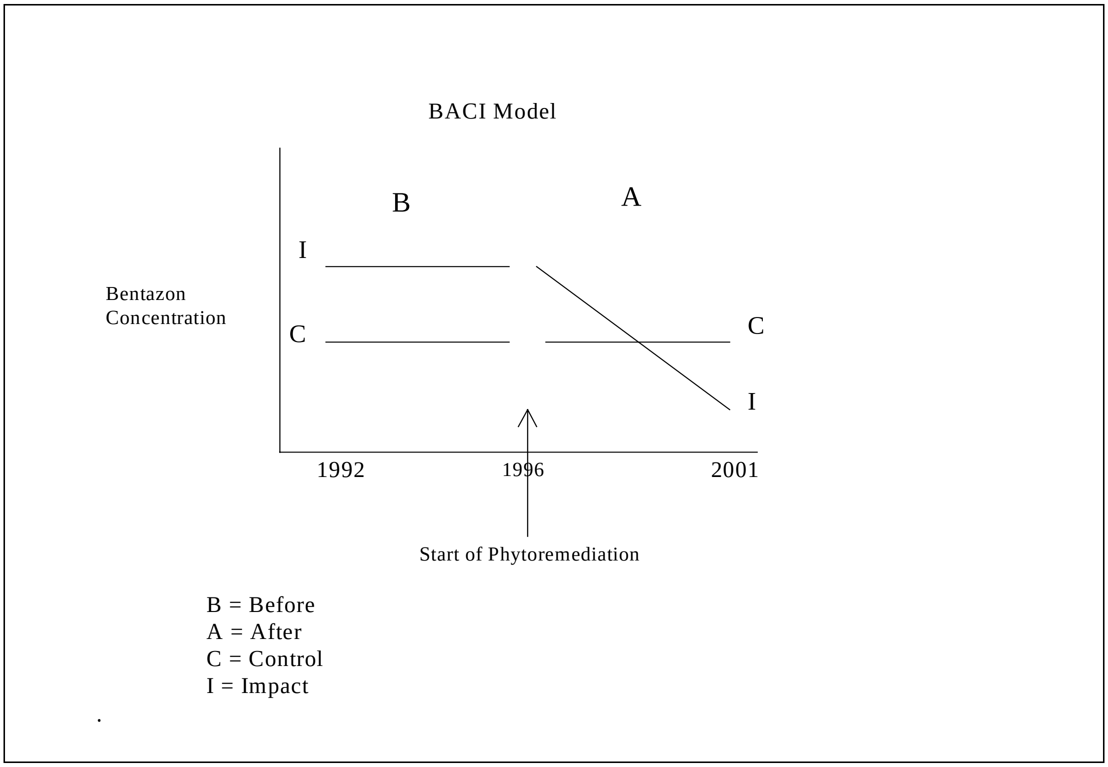


Figure 2.3: Before After Control Impact (BACI) Model as used at the Phytoremediation Test Site at BASF Corporation, Geismar, Louisiana (Smith, 2002).

CHAPTER 3: PHYSICAL AND CHEMICAL PROPERTIES OF THE PHYTOREMEDIATION TEST SITE

3.1 Phytoremediation Test Site Characteristics

This Chapter provides a concise characterization of the physical and chemical properties of the phytoremediation test site. The test site hydrogeology, soil morphology and chemistry, and climate are presented in the following sections of this chapter.

3.2 Hydrogeology

The characterization of the site began in 1991 with a groundwater assessment. Semi-annual groundwater monitoring has continued since July 1991. A Resource Conservation Recovery Act Facility Investigation was also performed in 1994 as required by the U.S. Environmental Protection Agency. Since 1991, 95 soil borings and 17 groundwater monitoring wells have been drilled in the vicinity of the site. On the bentazon test site, 44 soil borings and 16 groundwater monitoring wells have been drilled. These borings were drilled to depths as great as 45 meters below ground surface to characterize the site (Figure 3.1). Both studies have provided an adequate characterization of the site hydrogeology and delineation of the extent of contamination to proceed with remedial planning

The geology at the BASF Facility in Geismar is complicated by the Mississippi River's historical meanders. The river's recent alluvial deposition during the Holocene is evident in soil cores from the many borings drilled at the bentazon site. The generalized stratigraphic sequence at the bentazon site at BASF is depicted in Table 3.1. The Holocene consists of alternating series of silts, sands, clays and gravels that are commonly observed in the Mississippi River Valley. These sediments overlie the Pleistocene deposits, which are predominantly dense clays. These clays contain lesser amounts of discontinuous fine sands and silts. The lower portions of the Pleistocene are massive, coarse-grained sands and gravels with interbedded clays and silts. These sand and gravel units comprise the Norco and Gonzales Aquifers (Long, 1965).

At the bentazon site the stratigraphic relationship between the Holocene and Pleistocene is variable, due to the historical meander of the Mississippi River, which is observed as an erosion surface on the top of the Pleistocene clays. This surface represents the easternmost boundary of the Mississippi River embayment (Long, 1965). It has been filled during geologic time with younger Holocene alluvium at the bentazon site as illustrated in the generalized block diagram, Figure 3.2.

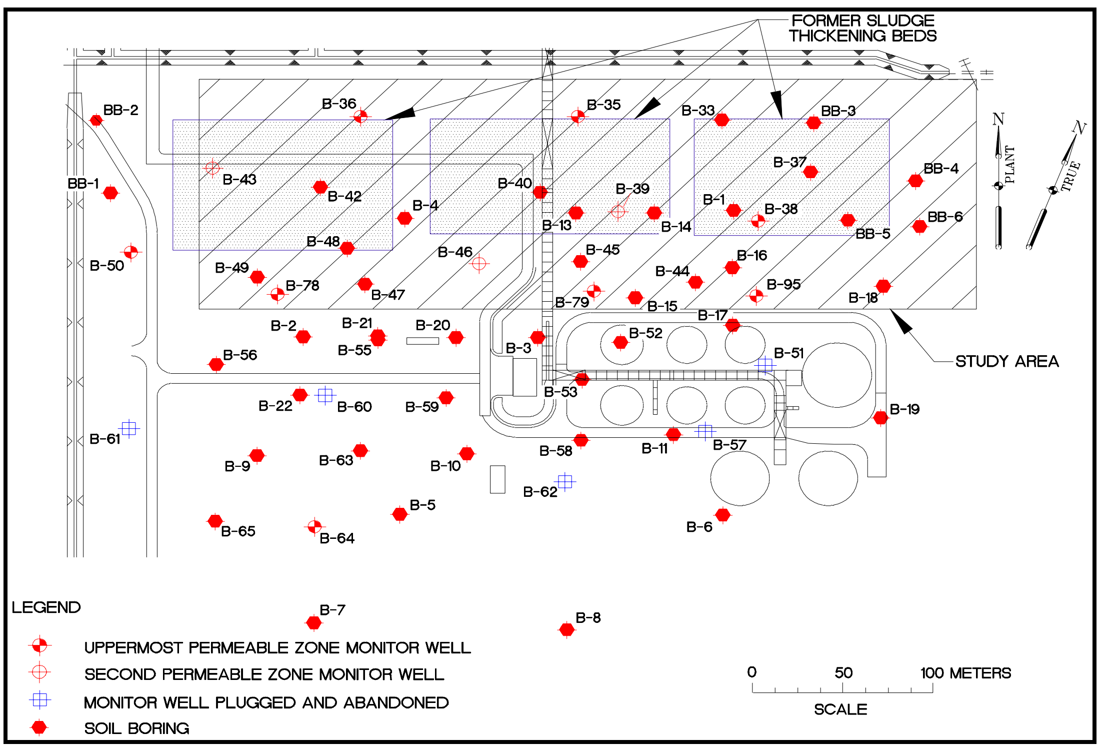


Figure 3.1: Soil Borings and Groundwater Well Locations Assessed at the BASF Phytoremediation Study Area

Table 3.1: Generalized Stratigraphic Sequence and Hydrologic Units, Geismar, Louisiana

GEOLOGIC UNIT	ZONE	DEPTH
Holocene	Upper	6 Meters
	Lower	15 Meters
Pleistocene	Clay Aquitard	15-80 Meters
	Norco Aquifer	80-113 Meters
	Gonzales Aquifer	134-198 Meters

(Woodward-Clyde Consultants, 1991)

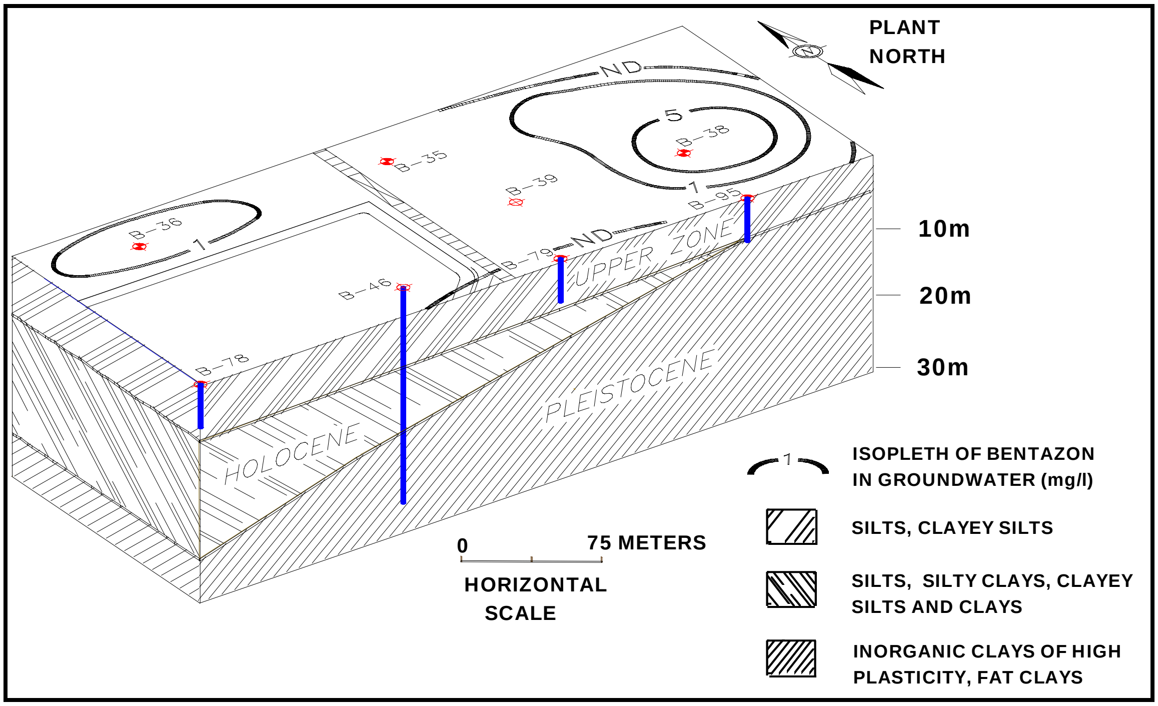


Figure 3.2: Subsurface Block Diagram of the Test Site Geology, Geismar, Louisiana

This meander feature also accounts for the great degree of heterogeneity in observed lithology of the shallow subsurface at the bentazon site. East of the meander line, the Holocene sediments are natural levee deposits that grade to backwater swamp deposits. Lithologies include silts and clays, with the latter becoming increasingly prominent in an eastward direction. Toward the west of the meander line, the stratigraphy encountered consists of a meander sequence including river channel, point bar, and oxbow lake deposits.

The lithologies are variable, dependent upon the source of origin from coarse sands in abandoned river channels that grade from fine sands in point bars to silts and soft organic clays in oxbow lake deposits. During the characterization of the bentazon site, no river channel or point bar sequences were encountered in any of the soil borings. However, previous work at the BASF Facility has identified such sediments at approximately 15 meters depth and 200 to 300 meters northwest of the bentazon site.

Holocene sediments are easily distinguished from Pleistocene sediments based on their texture, color, apparent strength, and organic content. Holocene sediments are fine-grained organic to silty clays that are commonly soft in consistency. They are much darker in color than Pleistocene sediments, as well. By contrast, the older underlying Pleistocene sediments are often comprised of stiff to hard clays with light tan and gray colors of thin, discontinuous, fine interbedded silts and sands. These sediments often have secondary features, such as iron and calcareous nodules, and slickened-sides that are characteristic of the Pleistocene. Organic content is very low in Pleistocene clays in this area.

Groundwater is commonly encountered at shallow depths near the surface at the bentazon site (Figure 3.3). A shallow zone of soft clays to slightly silty clays, with thin layers of clay silts or silts in the Holocene, has been delineated at the bentazon site as the first water-bearing zone. This zone is referred to as the Upper Zone and commonly occurs from near ground surface to about 6 meters in depth. The Lower Zone includes clay silts to silty clays at a depth of about 15 meters in the Holocene. At some depth greater than 45 meters and over 300 meters west, it is suspected that the Alluvial Aquifer is present. During the Late Pleistocene, the river eroded a broad valley into older deltaic deposits, which was subsequently refilled with gravel, clay, silt, and sand alluvial deposits. This is often referred to as the alluvium, and its boundary is referred to as the meander line. According to Long (1965), the Alluvial Aquifer is present within the recent alluvium along the eastern margin of the meander line. Since the characterization of the bentazon site began in 1991, the meander line has been delineated in a general north to south direction on the western side of the site. The Alluvial Aquifer has not been encountered by drilling during the site investigations conducted thus far.

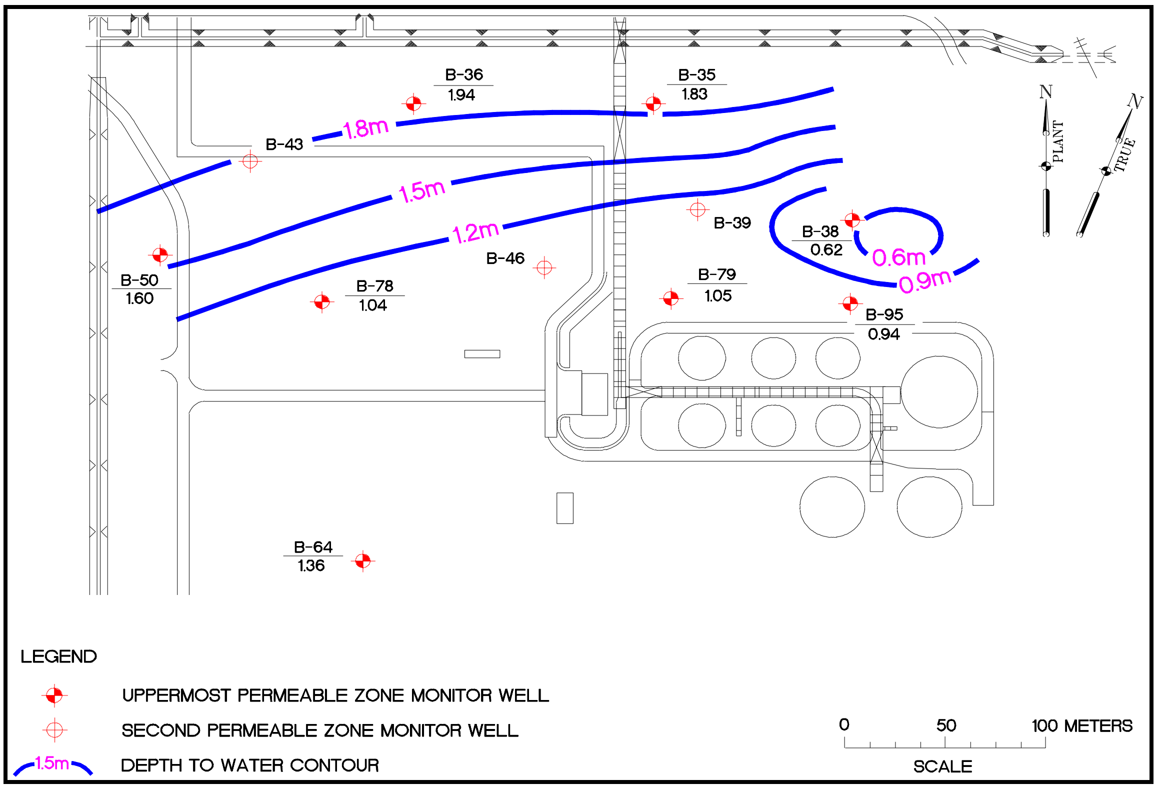


Figure 3.3: Map of the Depth to the Water Table, September 12, 1994 at the Test Site

The Pleistocene clays that underlie the Holocene have been found to extend from about 15 to about 80 meters in depth at the BASF Facility. These clays are not hydraulically confining, but act as an aquitard in a semi-confined system for the underlying Norco Aquifer west of the meander line. The Norco Aquifer consists of coarse-grained sands and gravels and is encountered from about 80 to 113 meters in depth at the BASF Facility. This aquifer is used in the Geismar area to supply rural residences and to provide industrial cooling water. Although it naturally exhibits poor aesthetic qualities, such as hardness and mineral impurities, that make it less desirable for consumption (Long, 1965), it was considered the first possible off-site human exposure route for contamination of groundwater.

The Gonzales Aquifer, which is the most important aquifer to the area, is the most common drinking water source for Ascension Parish and is found between about 134 to 198 meters in depth at the BASF Facility. The nearest receptor wells to the bentazon site are Gonzales Aquifer wells at the BASF Facility, about 1.5 kilometers from the bentazon site. The nearest known residential groundwater use from the Gonzales Aquifer is outside the BASF Facility. This is about 3 kilometers east of the bentazon site.

Figure 3.4 illustrates the groundwater elevation in the Upper Zone, as observed in September 1994 at the bentazon site. Groundwater flow is indicated to be northerly with a low hydraulic gradient that averages about 0.003 meter/meter (Woodward-Clyde Consultants, 1991). When combined with an average hydraulic conductivity of 4.94×10^{-4} centimeters/second and an effective porosity of 0.25, a horizontal groundwater velocity of 1.8 meters per year is estimated (Woodward-Clyde Consultants, 1991). Table 3.2 provides the actual hydraulic conductivity and transmissivity values from pumping tests for the Upper Zone. This low velocity suggests that, in normal conditions, groundwater flow is so slow that the bentazon dissolved in the shallow groundwater should pose no immediate migration risk from the site.

A plume of dissolved bentazon in the shallow groundwater within the Holocene sediments has been delineated. Groundwater concentrations observed at the bentazon site have been greatest between 1 to 7 milligrams per liter (mg/l) and in most wells below 1 mg/l. Figure 3.5 is an isoconcentration map of bentazon sampling data from the September 1994 sampling of the existing monitoring well network.

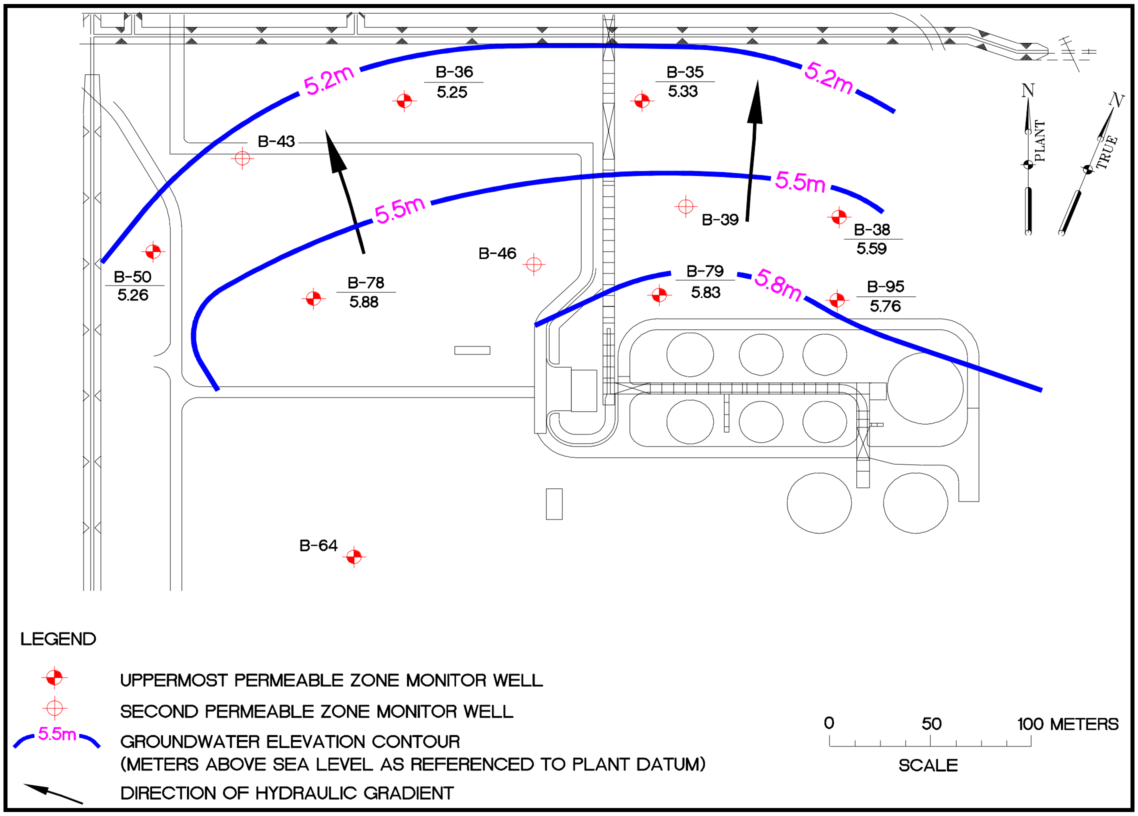


Figure 3.4: Potentiometric Surface Map of the Upper Zone, September 12, 1994 at the Test Site

Table 3.2. Hydrologic Properties Calculated from Pumping Tests, Shallow Holocene Zone

WELL	TRANSMISSIVITY	HYDRAULIC CONDUCTIVITY
B-36	$1.35\text{x}10^{-5}$ to $3.89\text{x}10^{-5}$ m^2/sec	$4.45\text{x}10^{-4}$ to $1.27\text{x}10^{-3}$ cm/sec
B-51	$3.17\text{x}10^{-6}$ to $9.36\text{x}10^{-6}$ m^2/sec	$2.05\text{x}10^{-4}$ to 6.14x 10^{-4} cm/sec
B-61	$2.45\text{x}10^{-6}$ to $6.48\text{x}10^{-6}$ m^2/sec	$8.11\text{x}10^{-5}$ to $2.12\text{x}10^{-4}$ cm/sec

(Woodward-Clyde Consultants, 1991)

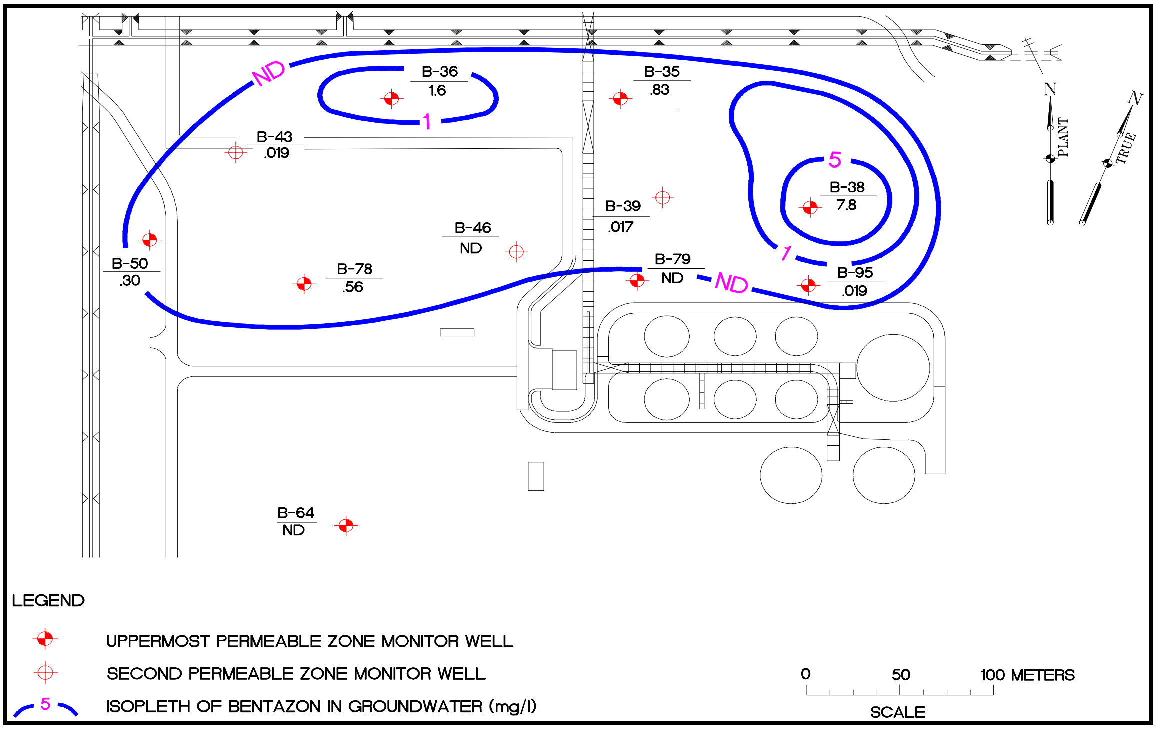


Figure 3.5: Isoconcentration Map of Bentazon in Groundwater from the Upper Zone at the Test Site in September 1994

The two groundwater monitoring wells that exhibited the greatest concentrations prior to phytoremediation, as detected by sampling results are illustrated on the September 1994 isoconcentration map. These bentazon-impacted wells, B-36 and B-38, are screened in the Upper Zone of the shallow Holocene about 5.5 meters below ground. The Upper Zone is contaminated and consists of a clayey silt to silty clay that is commonly encountered throughout the facility as the first water bearing zone, usually between depths of about 0.5 to 6 meters. The affected area, with concentrations above 1 mg/l, is approximately 4 to 5 hectares in size. One of the deeper wells, B-43, which is screened in the Lower Zone of the Holocene, has reported bentazon concentrations at less than 0.019 mg/l, which is not significant since this concentration is below the EPA’s health advisory level of 0.020 mg/l for bentazon.

3.3 Phytoremediation Test Plot Soil Morphology and Chemistry

The BASF test site was a sugar plantation and open cattle range prior to its development into a petrochemical facility. The property was initially cleared for agricultural use in the early 1800's by the William Kenner family as the Linwood sugar plantation (Bauer, 1993). It was kept in that capacity until the great flood of 1927 ruined sugar crops throughout the Mississippi River Valley and led to financial ruin for the landowners. Cattle farming was begun in the late 1940's on the property and continued until BASF's predecessor company, Wyandotte Chemical, purchased the property in 1955. Construction of the chemical facilities began the following year and development as a petrochemical production facility has continued since then. Soils in this area are highly productive as agricultural lands and rich in organic matter and nutrients from the riparian wetlands that preceded the plantation use of the property. The impact on the soil chemistry after over 150 years of agricultural use is uncertain.

The geomorphic features of the BASF property are heavily influenced by the Mississippi River and its agricultural development as a sugar plantation. Near the river, the land surface elevation is nearly 7 meters above sea level and drops in elevation away from the river to nearly 4.5 meters above sea level over a distance of less than 2.5 kilometers. The test area is approximately 500 meters east of the river at a surface elevation of between 5 to 6 meters above sea level. The change in surface topography is indicative of the natural levee to floodplain to backwater swamp transition commonly found throughout the Mississippi River Valley. This is also apparent from the change in soil texture from sands to silts to clays away from the river. Soils in the area of the test location are silty clays as previously described.

The original floodplain surface still includes former cane field drainage canals and cross-flow connecting shallow ditches, which have changed the original hydrology of the soils. According to the latest soil survey of the area (USDA, 1976), a large portion of the soils on the BASF Property are hydric soils of the Sharkey and Acy-Jeanerette Associations. The soils in the test plot areas are Acy-Jeanerette.

Eight random soil samples were collected monthly from twelve inches depth during the 1999 growing season at each test plot and analyzed for soil nutrients. These nutrients included phosphorus, sodium, potassium, magnesium, calcium, sulfur, copper, iron and manganese. These data are summarized in Tables 3.3 and 3.4.

Table 3.3: Summary of Soil Chemistry at Plot 1, 1999

Analyte	Mean (within 95% Confidence Interval)	Standard Error	Variance
pH	7.65 ± 0.11	0.052	0.1319
Phosphorus	481.8 ± 52.0	25.9	32081.9
Sodium	119.9 ± 78.0	38.8	72147.5
Potassium	368.3 ± 33.9	16.9	13641.9
Magnesium	401.9 ± 32.4	16.1	12427.5
Calcium	5842.7 ± 298.4	148.3	1056261
Sulfur	41.0 ± 15.7	7.69	1896.6
Copper	6.81 ± 1.04	0.51	8.3
Iron	76.9 ± 8.53	4.18	560.0
Manganese	9.42 ± 2.58	1.26	51.1
Zinc	6.0 ± 1.7	0.84	22.52

Results in mg/l, except for pH which is in standard units.

Table 3.4: Summary of Soil Chemistry at Plot 2, 1999

Analyte	Mean (within 95% Confidence Interval)	Standard Error	Variance
pH	7.8 ± 0.2	0.11	0.5811
Phosphorus	406.3 ± 67.5	33.5	54002.7
Sodium	686.1 ± 125.8	62.5	433.1
Potassium	774.8±217.0	107.9	558738.5
Magnesium	476.8±29.5	14.6	10301.2
Calcium	6296.4±539.0	267.9	3445470
Sulfur	324.8±116.5	57.1	104369.2
Copper	7.92±1.4	0.6771	14.7
Iron	91.1±13.7	6.7	1446.5
Manganese	8.5±1.1	0.541	9.4
Zinc	4.3±1.0	0.454	6.6

Results in mg/l, except for pH which is in standard units.

The summary suggests that soils are rich in magnesium, potassium and calcium, which were indicative of a basic soil. This was also supported by soil pH values, above 7. Other minerals important to microbial growth such as iron and sulfur were also in abundance. Potassium, phosphorus, and magnesium exhibit a greater degree of variability, but generally they too were very abundant. Calcium and sodium content was also very high in the soils at the test site. Comparing the means of calcium and sodium, Plot 2 was more abundant in these cations than Plot 1.

Sulfur and iron, which play important roles in nutrient cycling, were also very abundant. Table 3.5 provides a comparison with the commonly observed concentrations of these minerals in agriculture as provided by the Louisiana Cooperative Extension

Service (1999a). Copper, manganese and zinc concentrations were also abundant in the soils at the test site (LCES, 1999b).

Table 3.5: Comparison of Test Plot Sulfur and Extractable Metals to Agricultural Ratings (LCES, 1999a and 1999b)

Analyte	Plot 1	Plot 2	Agriculture Rating
Sulfur	41.0	324.8	>12 (High)
Copper	6.81	7.92	>0.25 (High)
Iron	76.9	91.9	>4.5 (High)
Manganese	9.4	8.5	>4.0 (High)
Zinc	6.0	4.3	>1.25 (High)

Soil samples were also taken from each plot and analyzed for Total Organic Carbon (TOC). Twelve individual samples of soil were taken from each of the two test plots in March 1998 to determine the concentration of organic carbon to derive a mean variable for use in groundwater modeling. Table 3.6 is a summary for this sampling. TOC concentrations are as would be expected in alluvial sediments.

In summary, soils at the test site are typical Mississippi River alluvium that were predominantly silty clays are abundant in nutrients that are used to evaluate agricultural potential. These soil nutrients sampled at both test plots do not indicate any anomaly that would suggest adverse effects upon the growth of the black willow at the test locations or to have any effect on bentazon concentrations in groundwater at the test site. Soil chemistry was not assumed to be an important environmental factor to phytoremediation effectiveness at this location.

Table 3.6: Soil Total Organic Content (%)

Sample	Plot 1	Plot 2
1	1.71	0.476
2	0.824	1.24
3	1.06	0.773
4	0.514	1.15
5	0.492	0.51
6	9.48	0.747
7	2.64	0.699
8	0.483	0.963
9	1.21	0.971
10	0.628	0.969
11	0.785	1.02
12	1.58	1.13
Mean within 95% Confidence Interval	1.783 ±1.592	0.887±0.156
Standard Error	0.723	0.071
Sample Variance	6.281	0.060

3.4 Regional and Local Climate Suitability for Phytoremediation

The climate of any area selected for phytoremediation can play a significant role in whether the technique will succeed or fail, because a selected plant must be capable of sustaining itself in the selected climate. Geographic regions that are devoid of vegetation due to climate (lack of water, insufficient light, or the unsuitable temperature ranges for the more desirable phreatophytic species) are obviously poor sites for phytoremediation.

Other environmental effects can have a positive effect on a contaminated site that could be misinterpreted as the effect of phytoremediation. This could include climatic conditions. As previously mentioned in Chapter 2, meteorological data were recorded with a portable weather station using a computerized datalogger on a 24-hour basis. Rainfall, soil temperature, surface temperature, and air temperature were principal conditions recorded; wind speed and direction, solar radiation, and relative humidity were collected as secondary data. Evapotranspiration was calculated from the data by the

Penman (1948) method. During each of the six experiments in 1998 and the twelve experiments in 1999, the weather station was operated concurrently. Figure 3.6 illustrates a sample of the meteorology data collected during the course of an experiment in 1998. The figure illustrates the expected diurnal pattern of daily cycles of solar energy and corresponding surface temperature and humidity.

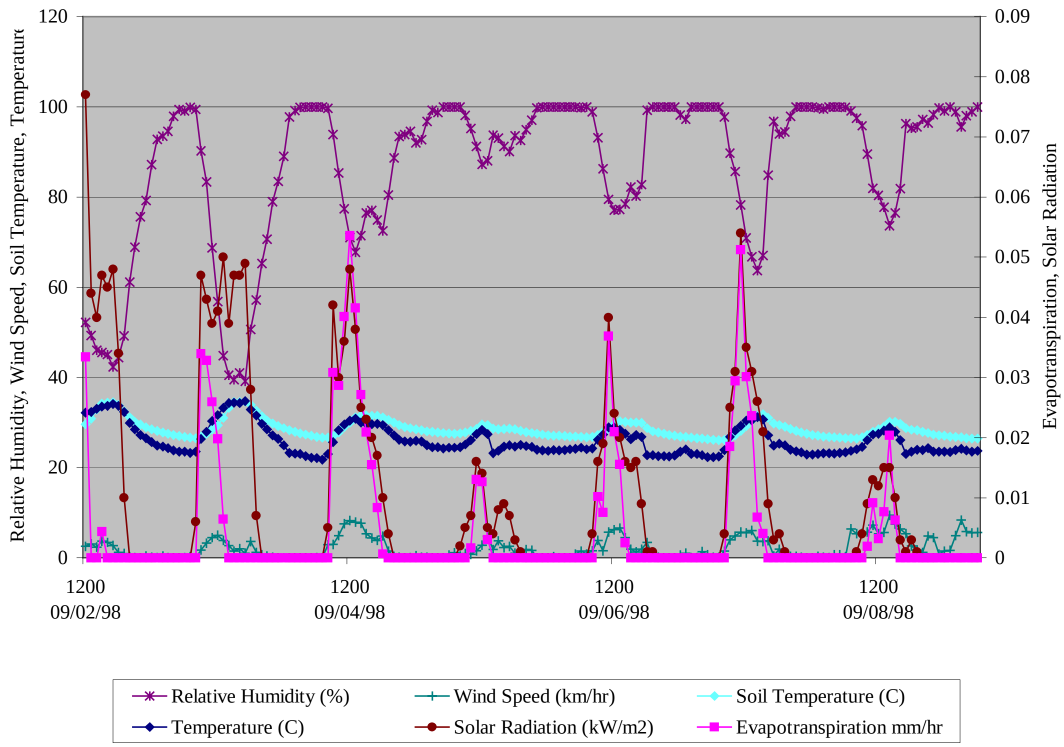


Figure 3.6: Meteorological Conditions Recorded during Experiment 5 at Plot 2, September 2-9, 1998 (Note: Diurnal pattern evident in meteorology)

To compare weather condition observations during the sap flow tests, existing weather databases were sought out. The nearest National Oceanic and Atmospheric Administration weather station to the BASF Site that is monitored continuously is the Carville, Louisiana Station about 13 kilometers north. The annual climatological data summaries for 1998 and 1999 were reviewed to obtain the Carville data (NCDC, 1998 and NCDC, 1999). The surface temperature, soil temperature, evapotranspiration, and rainfall for the growing seasons of 1998 and 1999 were obtained from the Carville Station and compared to the test location weather station data. These data are summarized on a monthly average basis for the entire 1998 and 1999 growing season months of April through September in Table 3.8. The data generally correlated from both the Carville Station and the test location. Two observations are noted concerning this generalized comparison. First, the surface and soil temperatures between Carville and the test location were within the expected deviation ranges noted in the annual summaries. Second, evapotranspiration and rainfall between the two stations are very similar. It should be noted that both these two years had lower than expected rainfall, while maintaining generally the same evapotranspiration rate. This would appear to support that there was less rainfall available for vegetation during the period observed, thus requiring the vegetation to rely on the water table in storage. In order to compare these observations graphically, Figures 3.7, 3.8, 3.9, and 3.10 illustrate all four variables. The generalized trends between the test location, the Carville station and the regional station do not suggest any observed anomalies from the historical data.

There were insufficient data to statistically analyze the meteorology for testing hypotheses. However, from qualitative observation, there were no obvious meteorological variables that suggest trends that could have effected the outcome of the phytoremediation test site in either a negative or positive manner. Conditions reported from the NOAA weather station at Carville appear to be as expected for this climate with only slightly less than normal rainfall.

Table 3.7: Summary of Meteorological Conditions during 1998-1999
(Temperatures in Celsius, Evaporation and Rainfall in Millimeters)

Condition	Monthly Average During Growing Season 1998/1999	Deviation from Historical Average During Growing Season 1998/1999
Temperature at Carville, La.	28.1/25.6	1.5/0.7
Temperature at Test Site	28.2/25.9	Not Available
Regional Soil Temperature	34.0/32.1	Not Available
Soil Temperature at Test Site	30.1/28.4	Not Available
Regional Evaporation	160.0/162.5	Not Available
Evapotranspiration at Test Site	166.3/144.8	Not Available
Rainfall at Carville, La.	561.3/613.4	-73.2/-110.2
Rainfall at BASF	402.6/573.8	Not Available

(NCDC, 1998 and 1999)

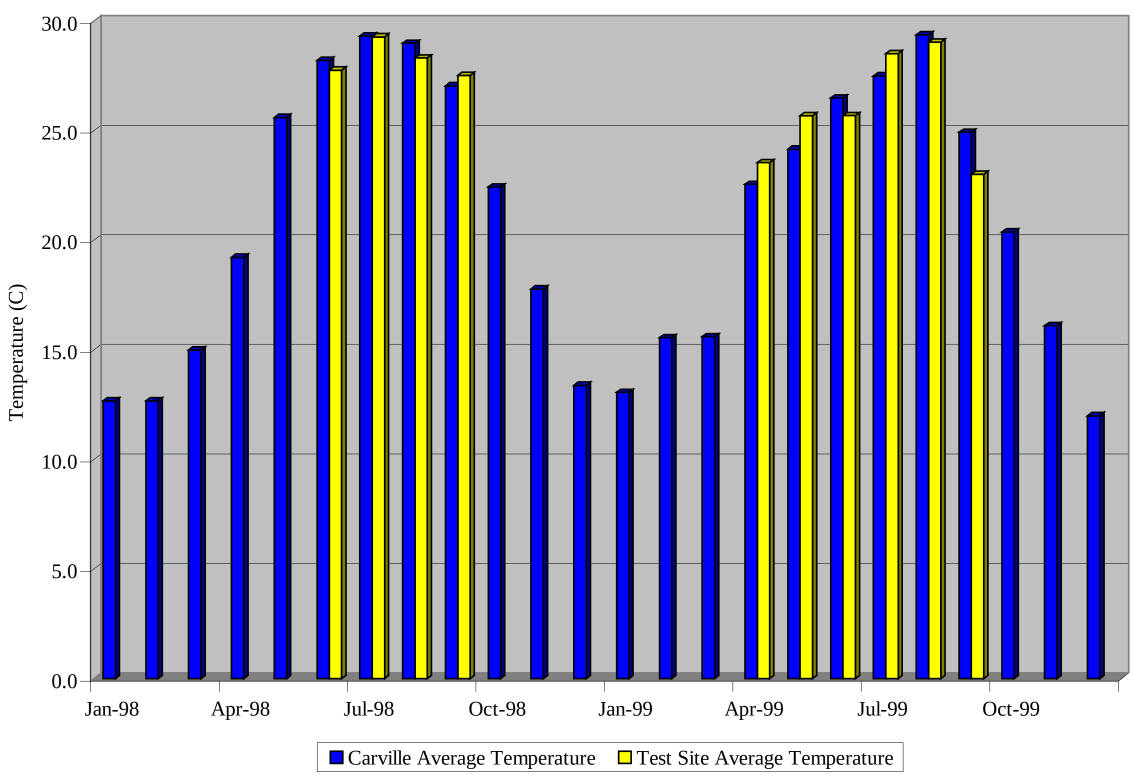


Figure 3.7: Average Monthly Surface Temperature at Carville, Louisiana and the BASF Test Site

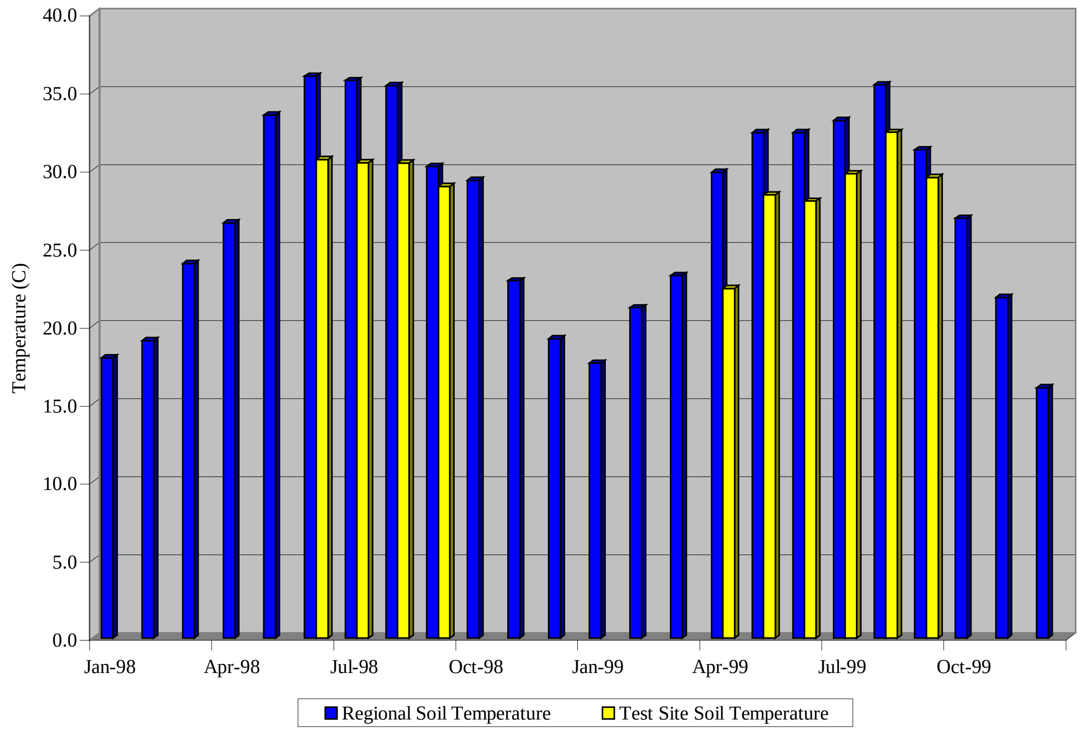


Figure 3.8: Average Monthly Soil Temperature Southeastern Louisiana and the BASF Test Site

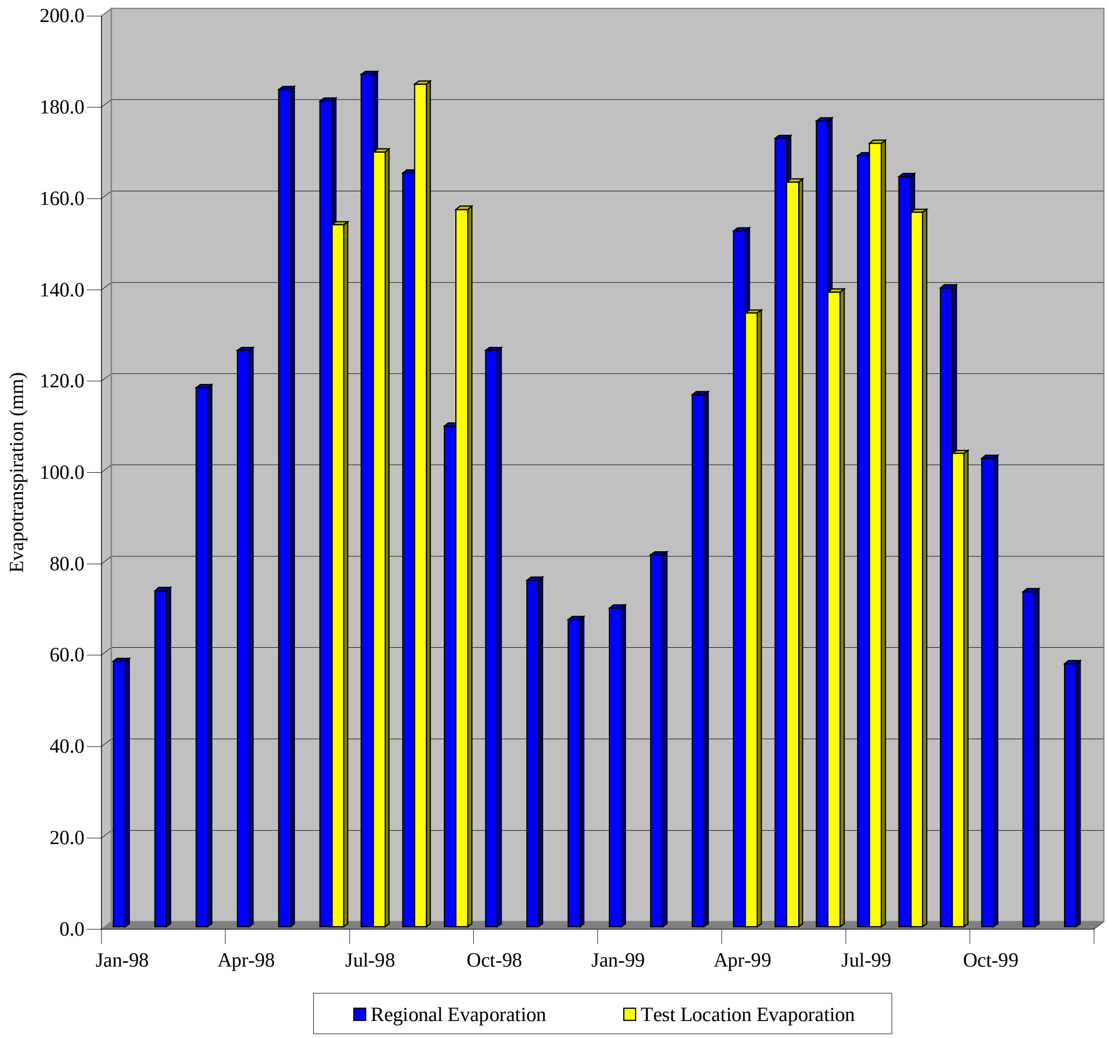


Figure 3.9: Average Monthly Evapotranspiration for Southeastern Louisiana and the BASF Test Site

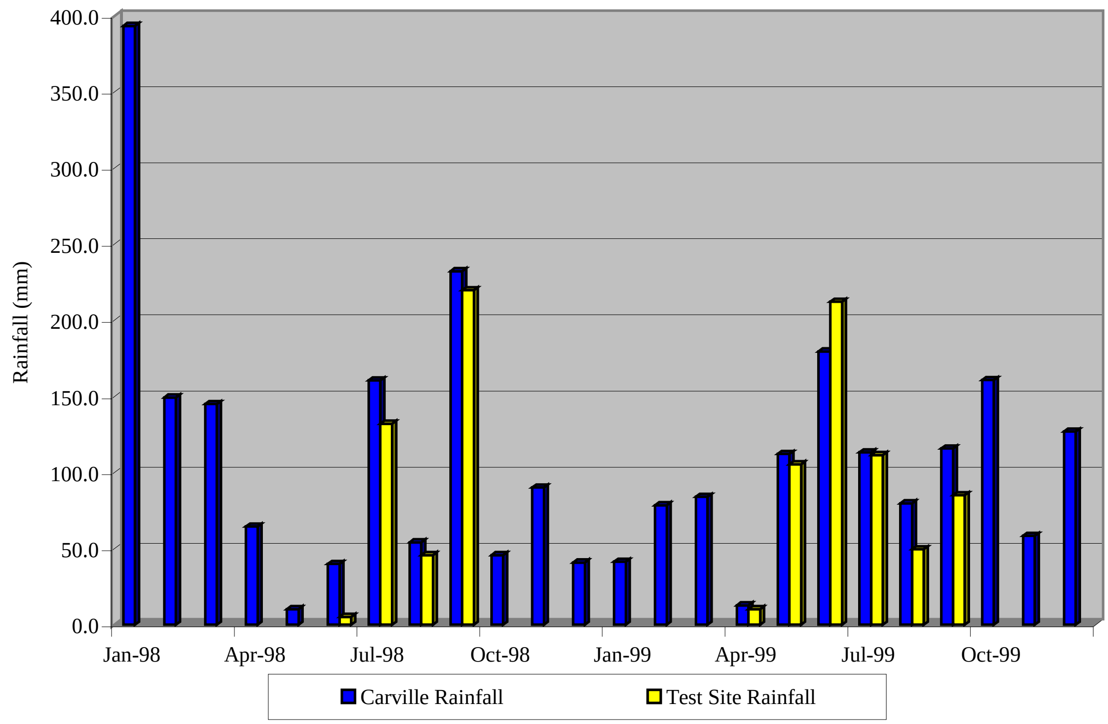


Figure 3.10: Average Monthly Rainfall for Carville, Louisiana and the BASF Test Site

CHAPTER 4: RESULTS OF PHYTOREMEDIATION RESEARCH

4.1 Phytoremediation Research Results

This chapter provides a discussion of the results and findings of the research performed to accomplish the objectives set out by this project, including the project goal to document and verify the success of phytoremediation at an industrial area of riparian wetland.

4.2 Test Plot Water Use and Growth Measurements

Several mechanical difficulties were encountered during the initial experiments in 1998 with the tree-trunk heat balance method. The computer loggers failed to collect data during the first four experiments on the second eight stem gauges, thus decreasing the sample set from 16 to 8. Stem gauge failures due to the interference of dewpoint moisture, imperfect apparatus field installation, and electrical shorts from moisture effects on the cabling further lessened the sample count. The stem gauge manufacturer responded to the equipment problems, and field adjustments to the equipment and installations were made. The last three experiments during 1998 yielded better results, as the number of samples collected were increased significantly. During the 1999 series of experiments, mechanical difficulties were minimized using the experiences of 1998.

An alternating diurnal pattern of sap flow was observed. Peak transpiration occurred during the early afternoon period with minimal transpiration from late evening until early morning (Figure 4.1). During daylight hours, the willow trees began to transpire as the stomata on the leaves opened to release water vapor. Osmotic pressure draws sap through the conductive sapwood from the roots up the trunk to the leaves. Subsequently, beginning at sundown, as photosynthesis ceases with decreasing light, the stomata close and transpiration ceases. Potential evapotranspiration follows the same trend. This is also correlated with relative humidity (Figure 4.2) and mimics the same diurnal pattern observed for transpiration. During periods of higher relative humidity, transpiration is lowest. Transpiration totally ceased when relative humidity reached 100%. This condition has been directly related to both stomatal response and evaporative demand (Meinzer et al., 1993). The availability of light, which is required for photosynthesis, is likewise required for transpiration to occur.

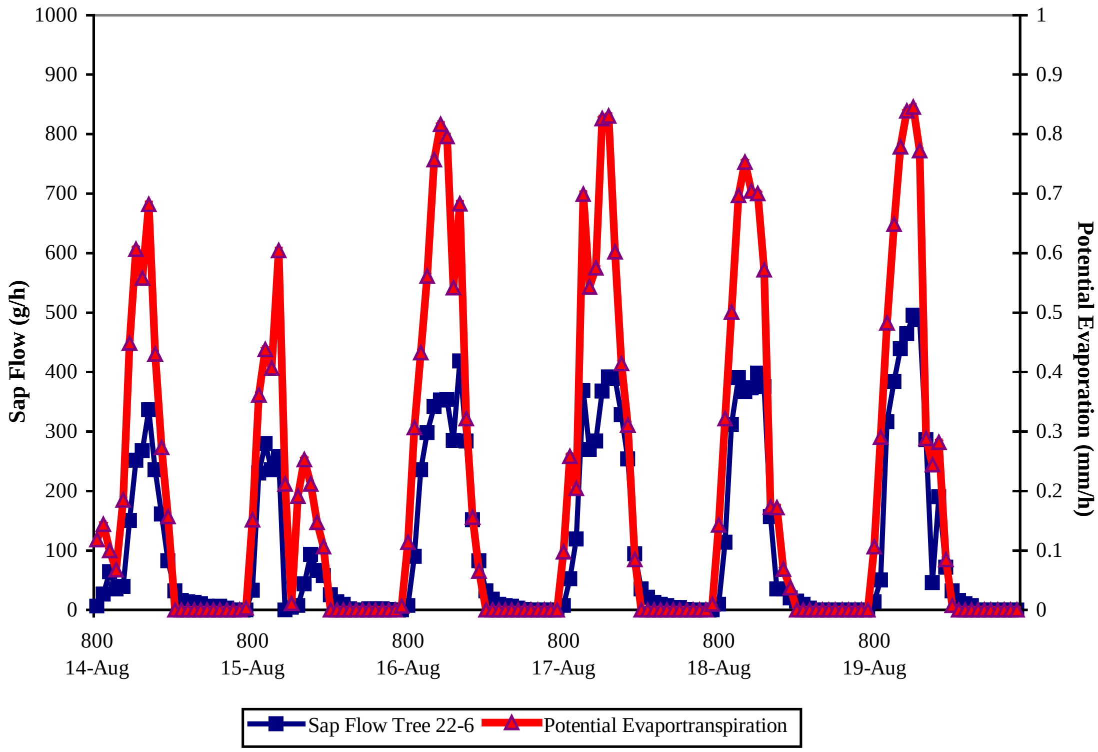


Figure 4.1: Sap Flow by Tree-Trunk Heat Balance Method, August 13-20, 1998

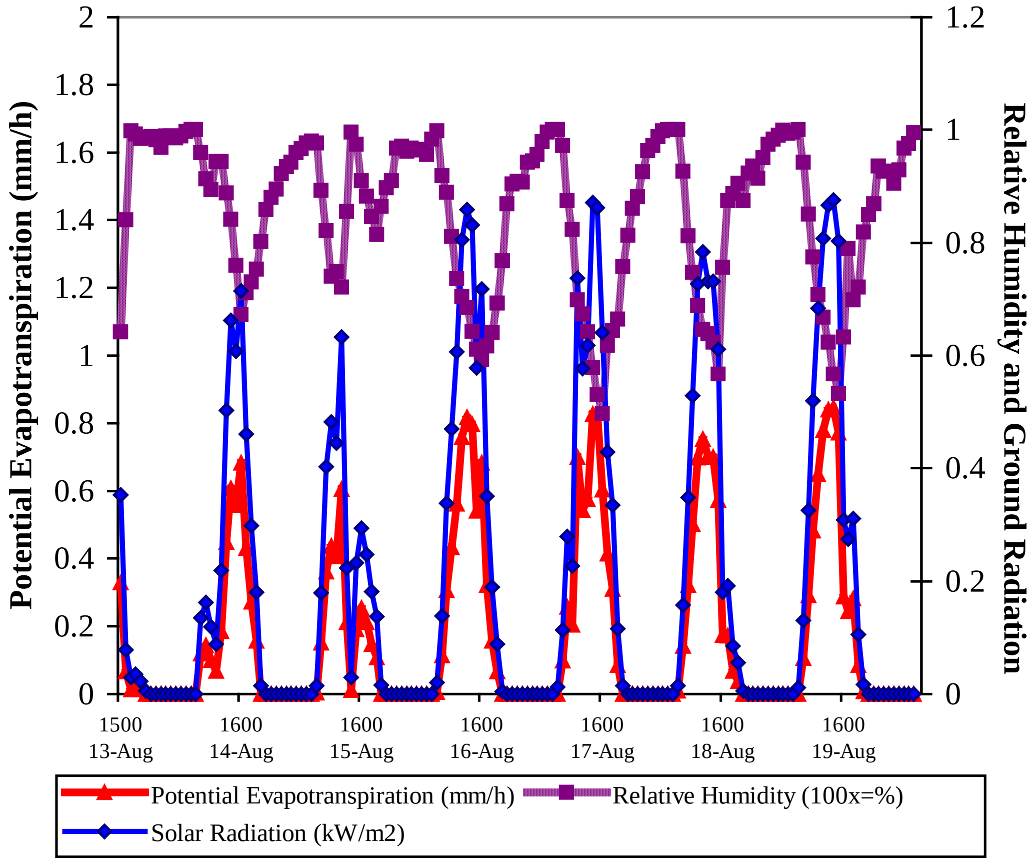


Figure 4.2: Relative Humidity, Potential Evapotranspiration and Sunlight, Plot 2, Experiment 4, August 14-20, 1998

Tabulations of the mean daily sap flow per unit area from each successful sample collection point in Plot 1 and Plot 2 were made. Table 4.1 provides the results of the 1998 sap flow experiments and Table 4.2 the 1999 sap flow results. During 1998, mean daily sap flow per unit area was 958 ml/day/cm^2 in Plot 1 and 1137 ml/day/cm^2 in Plot 2. The 1999-growing season experienced mean daily sap flow per unit area of 569 ml/day/cm^2 in Plot 1 and 838 ml/day/cm^2 in Plot 2.

Table 4.1: Results of Sap Flow Experiments during 1998

Plot 1 (438 Trees)	Jun-98	Jul-98	Aug-98	Sep-98	Averages
Sb= Sum of Basal Stem Area (cm^2)	6305	8743	11335	16000	10596
Growth Increase (%)		28	23	29	61
P_a= Plot Area (m^2)	1000	1000	1000	1000	1000
F_m=Mean Flow (ml/day/cm^2)	797	1354	1051	628	958
W= Water Use (ml/day/m^2)= (Sb x F_m) / P_a	5028	11842	11910	10051	9708
W in l/day/m^2	5	12	12	10	10
Cumulative Use (Liters)	5028	16870	28780	38830	

Plot 2 (1000 Trees)	Jun-98	Jul-98	Aug-98	Sep-98	Averages
Sb= Sum of Basal Stem Area (cm^2)	9317	14221	18173	21656	15842
Growth Increase (%)		34	22	16	57
P_a= Plot Area (m^2)	3000	3000	3000	3000	3000
F_m=Mean Flow (ml/day/cm^2)	1066	1735	935	811	1137
W= Water Use (ml/day/m^2)= (Sb x F_m) / P_a	3310	8222	5663	5856	5763
W in l/day/m^2	3	8	6	6	6
Cumulative Use (Liters)	3310	11532	17194	23050	

Table 4.2: Results of Sap Flow Experiments during 1999

Plot 1 (438 Trees)	Apr-99	May-99	Jun-99	Jul-99	Aug-99	Sep-99	Ave
Sb= Sum of Basal Stem Area (cm^2)	15957	16173	19602	22570	24430	26699	20905
Growth Increase (%)		1	17	13	8	8	40
Pa= Plot Area (m^2)	1000	1000	1000	1000	1000	1000	1000
Fm=Mean Flow (ml/day/cm^2)	866	559	281	769	675	265	569
W= Water Use (ml/day/m2)= (Sb x Fm) / Pa	13811	9034	5499	17345	16501	7088	11546
W in l/day/m^2	14	9	5	17	17	7	12
Cumulative Use (Liters)	13811	22845	28344	45689	52777	69278	

Plot 2 (1000 Trees)	Apr-99	May-99	Jun-99	Jul-99	Aug-99	Sep-99	Ave
Sb= Sum of Basal Stem Area (cm^2)	32469	35624	42913	48611	50922	51985	43754
Growth Increase (%)		9	17	12	5	2	38
Pa= Plot Area (m^2)	3000	3000	3000	3000	3000	3000	3000
Fm=Mean Flow (ml/day/cm^2)	599	830	1040	814	606	1139	838
W= Water Use (ml/day/m2)= (Sb x Fm) / Pa	6486	9850	14873	13187	10292	19731	12403
W in l/day/m^2	3	10	15	13	10	20	12
Cumulative Use (Liters)	6486	16336	31209	44396	64127	74419	

The sap flow measurements were standardized to the corresponding stem area to obtain a per unit area transpiration rate. This rate was used to calculate a mean plot flow measurement for each month during the 1998 and 1999 growing seasons. Figures 4.3 and 4.4 depict the monthly water use and tree stem growth for each plot during 1998 and 1999. The resulting mean daily plot flow was calculated at 10 l/day/m^2 in Plot 1 and 6 l/day/m^2 in Plot 2 during 1998, while in 1999, the mean daily plot flow was calculated at 12 l/day/m^2 , in both plots.

To put these data into usable form for groundwater modeling over longer periods of time, the maximum achievable canopy height had to be determined for black willow at the BASF facility. The height of the tallest indigenous black willows on the property was estimated to be 20 meters tall. The Plot 1 trees were maintained by pruning to a controlled height of 9 meters due to nearby electrical supply lines. The Plot 2 trees were on the average of 7.5 meters tall in 1999 and were nearly 12 meters tall as of May 2001.

Tree growth rates were calculated from actual stem thickness measurements obtained from each tree in each plot during each month of the growing season in 1998 and 1999. During 1998, the available stem area grew at 61% in Plot 1 and 57% in Plot 2. During 1999, smaller growth rates of 40% in Plot 1 and 38% in Plot 2 were experienced. This would be expected as the trees naturally slow in growth as they approach the maximum expected height of 20 meters. Since the Plot 1 trees are held at 9 meters height, water use is now estimated to be constant at the 12 l/day/m^2 rate or 3.6×10^6 liters per growing season. This is based on a 277-day growing season as established by the U.S. Soil Conservation service (USDA, 1976). Plot 2 was measured to have a tree canopy height of 10.5 meters in 2001, corresponding to slightly more than 50% of maturity expected 20 meters height. The water use in Plot 2 was estimated at 13.7 l/day/m^2 rate or 11.39 x 10^6 liters per growing season based on this.

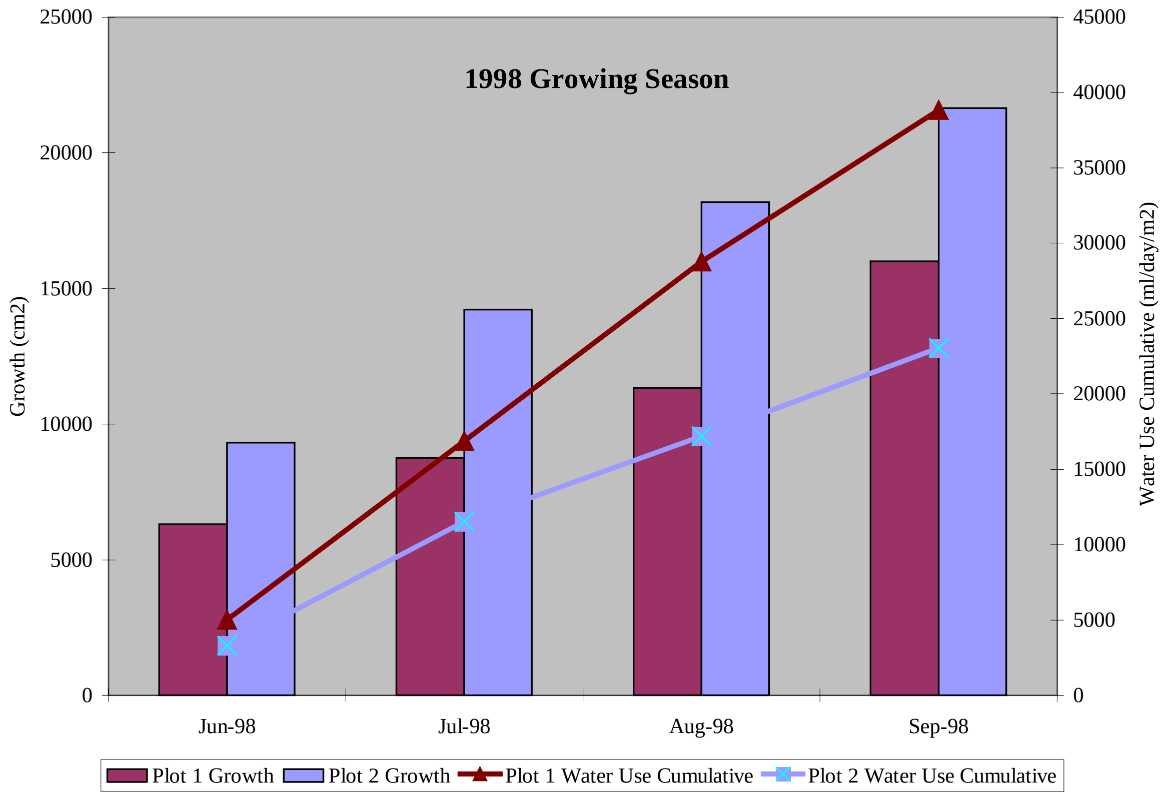


Figure 4.3: 1998 Water Use and Tree Growth Phytoremediation Plots 1 and 2

4.3 Modeling of Bentazon Transport and Fate in Groundwater

Groundwater modeling required initial calibration of the steady state and transient state flow conditions before solute transport modeling could be performed. This required the input of the observed potentiometric surface or head for known observation points at the outset of phytoremediation. As previously mentioned, January 1997 was used as the first time step in this model; therefore, this observed potentiometric surface was used. The calibration of steady state conditions, which represents static conditions, is illustrated in Figure 4.5. This is a comparison of observed potentiometric surface contours to the modeled potentiometric surface contours by overlaying them on the same map. To evaluate the accuracy of this calibration, Figure 4.6 is a graph of the observation point values versus the model value for the same locations. A regression of the data indicates an r^2 of 0.82. A value of 1.00 would indicate perfect correlation. The mean error calculated for this correlation was -0.0126 meters with a standard error of the estimate of 0.034 meters. These data suggest that the steady state calibration is valid.

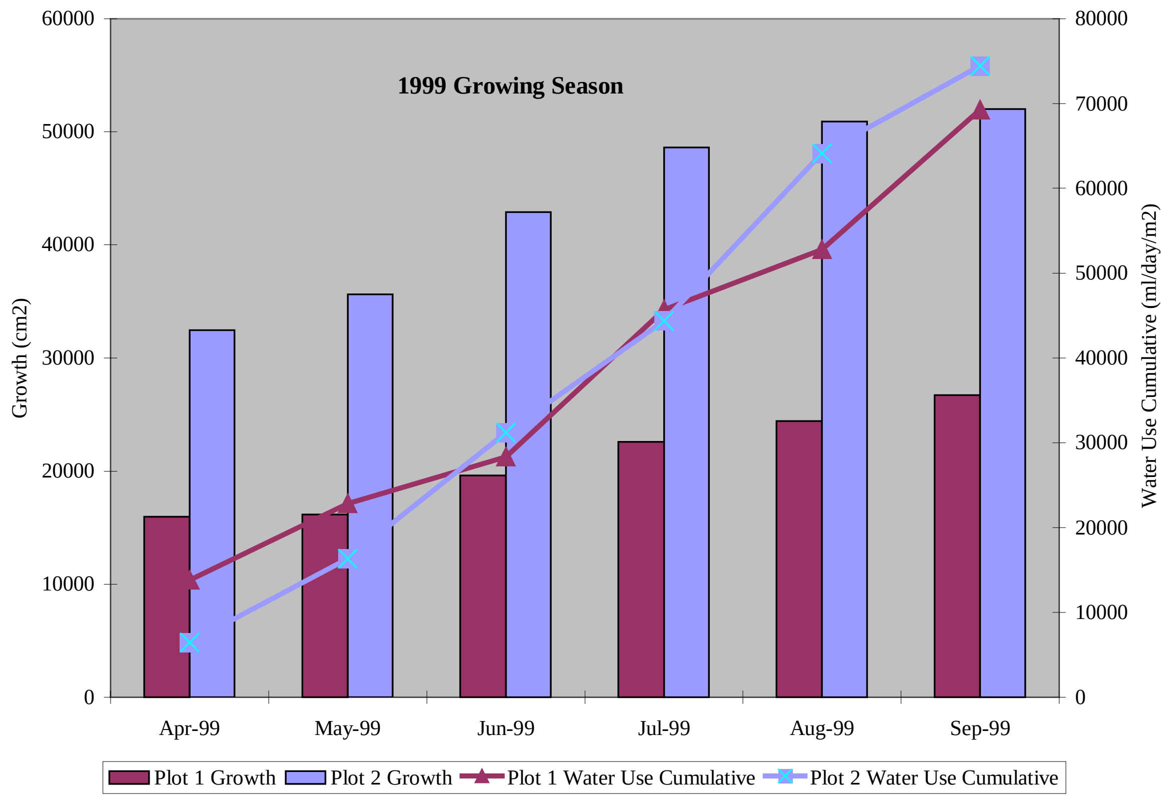


Figure 4.4: 1999 Water Use and Tree Growth Phytoremediation Plots 1 and 2

A transient calibration of the unsteady flow components was performed in a similar way. Figure 4.7 depicts the transient flow calibration map comparing the observed potentiometric head to the modeled potentiometric head. As in the steady state calibration, a graph of the observation point values to the model values is plotted in Figure 4.8. The regression of the data indicates a r^2 of 0.85. The mean error was -0.01372 meters with a standard error of the estimate of 0.01234 meters. These data likewise support that the transient calibration is valid.

The final modeling exercise was to run the solute transport engine of the model and to predict the reasonable amount of time needed to phytoremediate the bentazon concentrations in the groundwater. The transport evaluation was run at 5, 10, 20, and 22 years. Figures 4.9, 4.10, 4.11, and 4.12, illustrate a continuing decline in concentration of bentazon after each successive time interval. An endpoint concentration of 18 ug/l was used since that is the groundwater maximum contaminant level as set by the Environmental Protection Agency (USEPA, 1988) .The resulting model predicted that all bentazon concentrations would be below 18 ug/l after 22 years of phytoremediation. The contaminated area would below 18ug/l after the year 2018 based on this prediction.

The groundwater model predicts a favorable outcome within 22 years after phytoremediation started. However, another key objective of the study was to evaluate the migration potential of the bentazon. The groundwater solute transport predicts that migration from the phytoremediation plot areas of bentazon should not be possible.

4.4 Bentazon Concentrations in Groundwater Before and After Phytoremediation

To evaluate the progress of phytoremediation and its effectiveness at the test site, groundwater was monitored for bentazon concentration. As explained in Chapter 2, a Before After Control Impact (BACI) model (Smith, 2002) was used to evaluate data and hypotheses. Figure 4.13 illustrates the conceptual model as it was applied to this phytoremediation study. In order to formulate hypotheses with this model on expected trends, isoconcentration maps and line graphs of the well data were prepared.

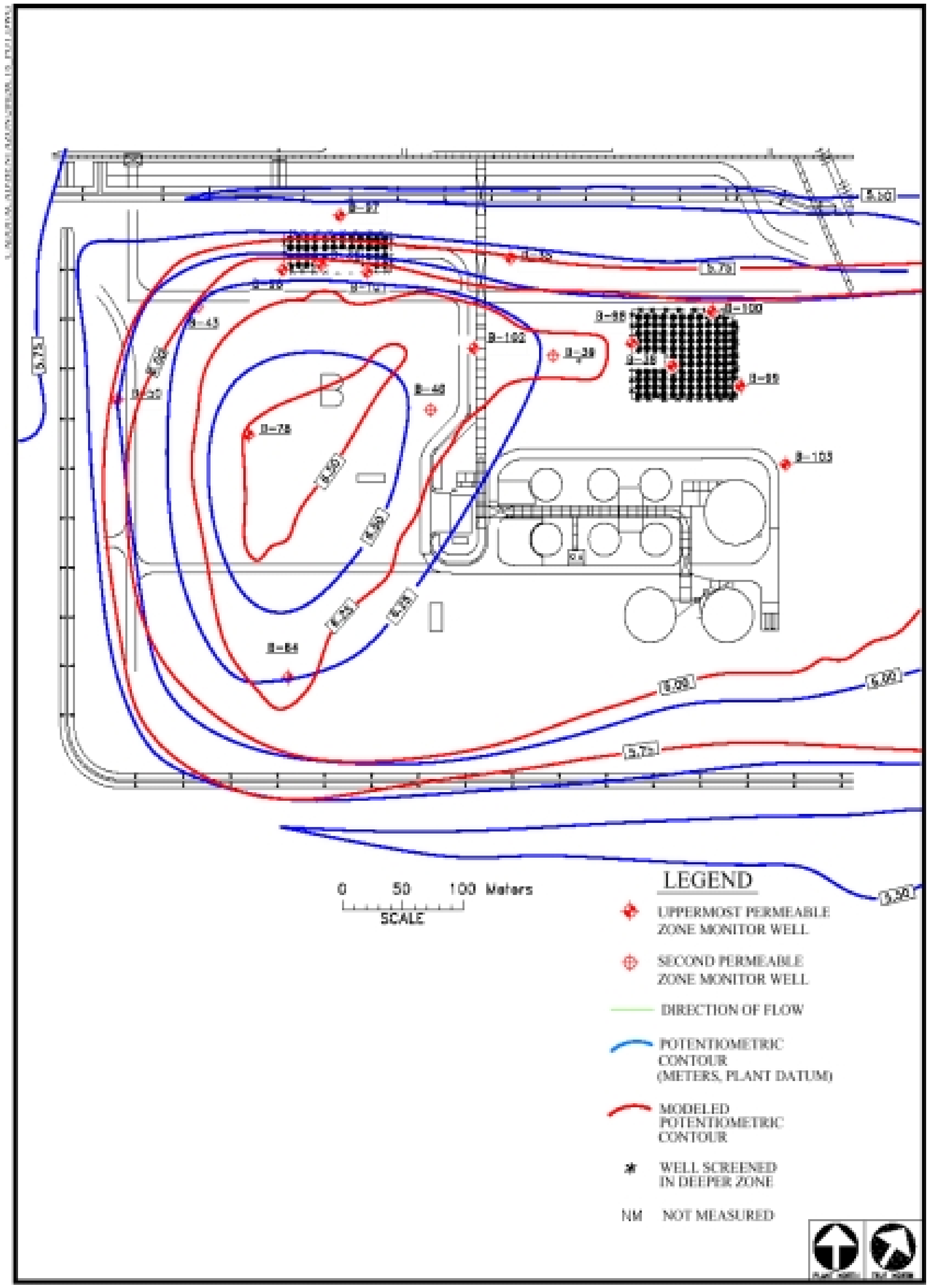


Figure 4.5: Steady State Groundwater Flow Calibration Map of BASF Test Plots

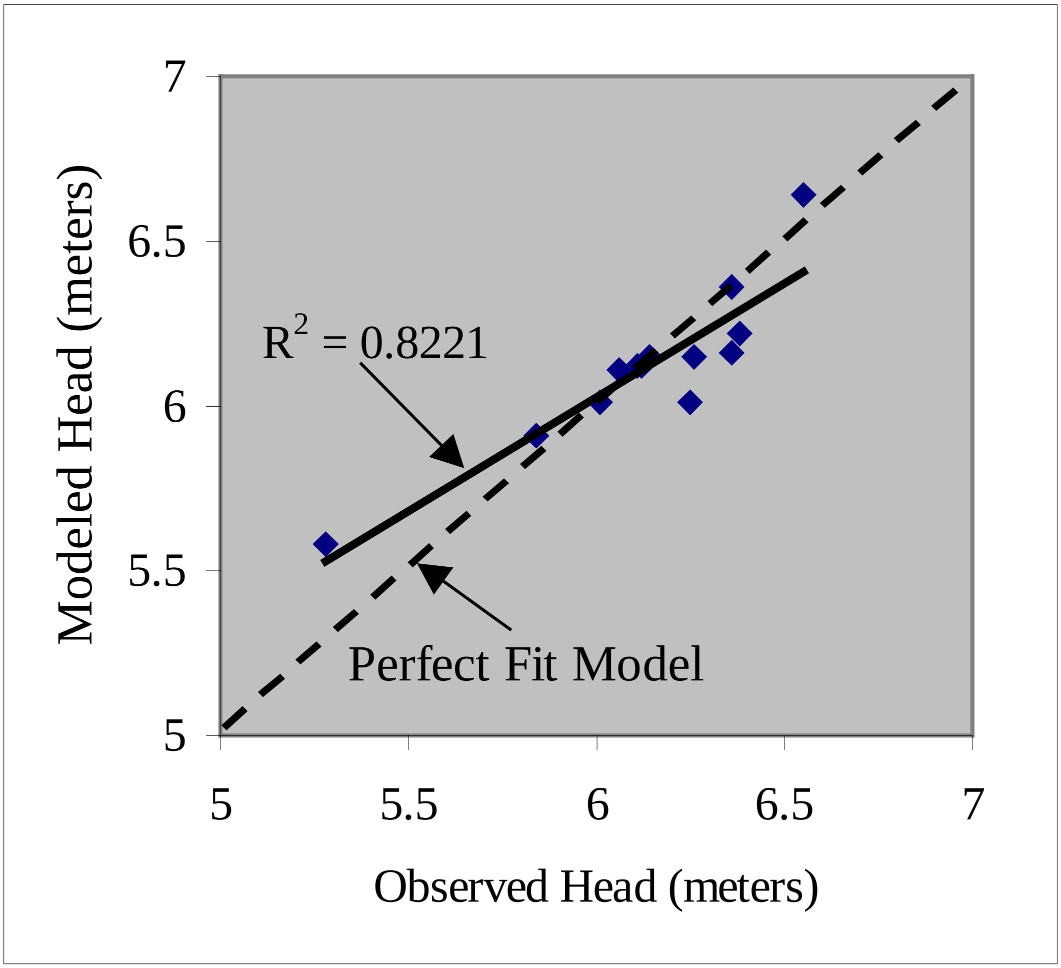


Figure 4.6: Plot of the Modeled Head Versus the Observed Head for the Steady State Model Calibration

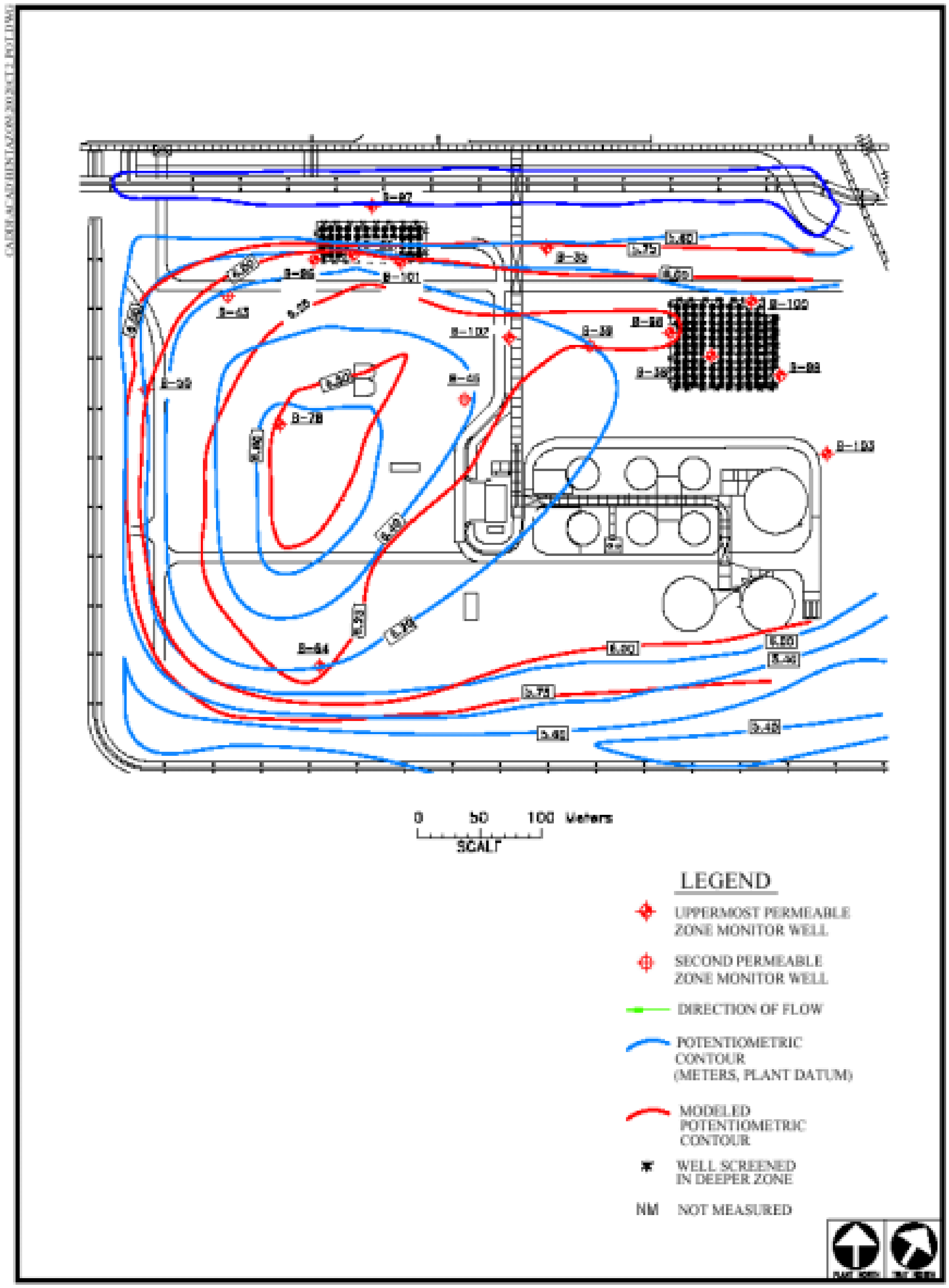


Figure 4.7: Transient Groundwater Flow Calibration Map of BASF Test Plots.

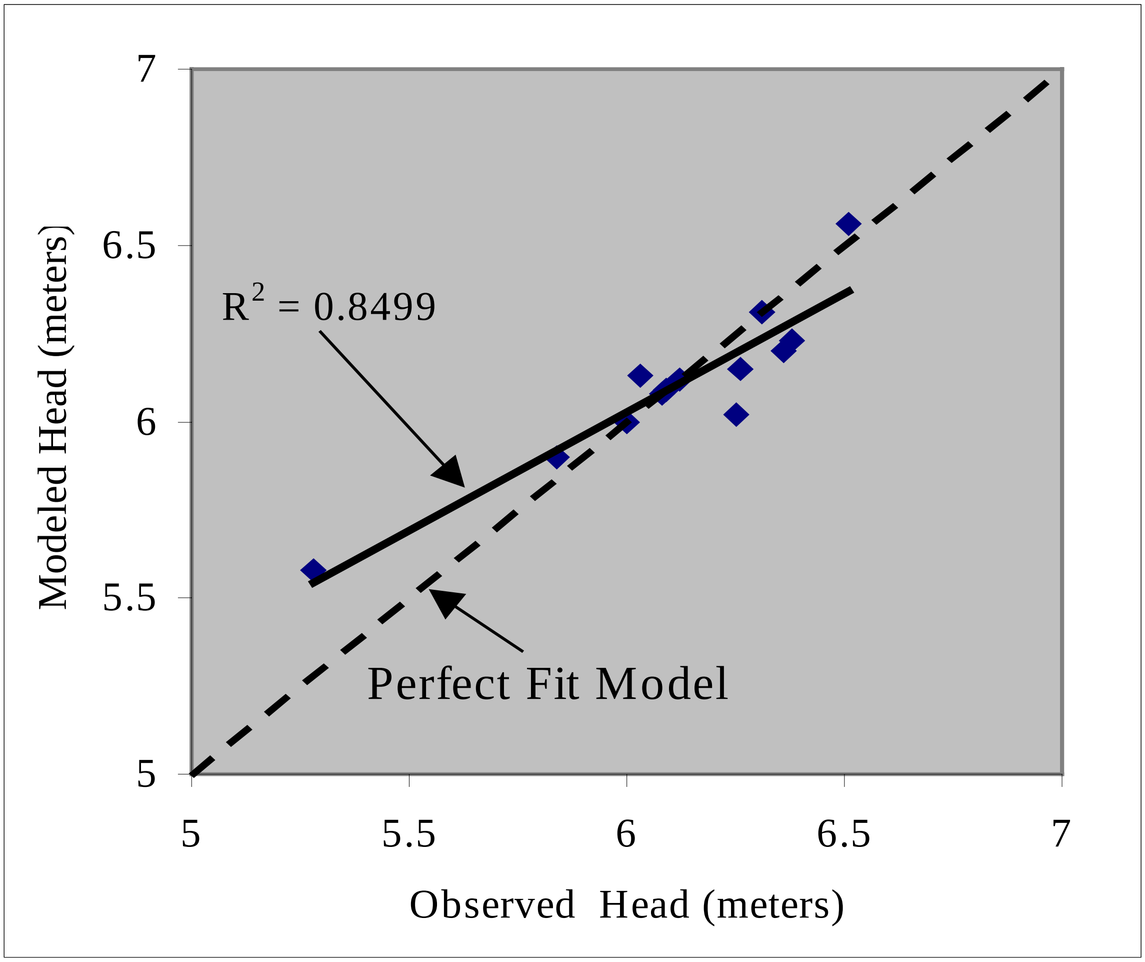


Figure 4.8: Plot of the Modeled Head Versus the Observed Head for the Transient Model Calibration

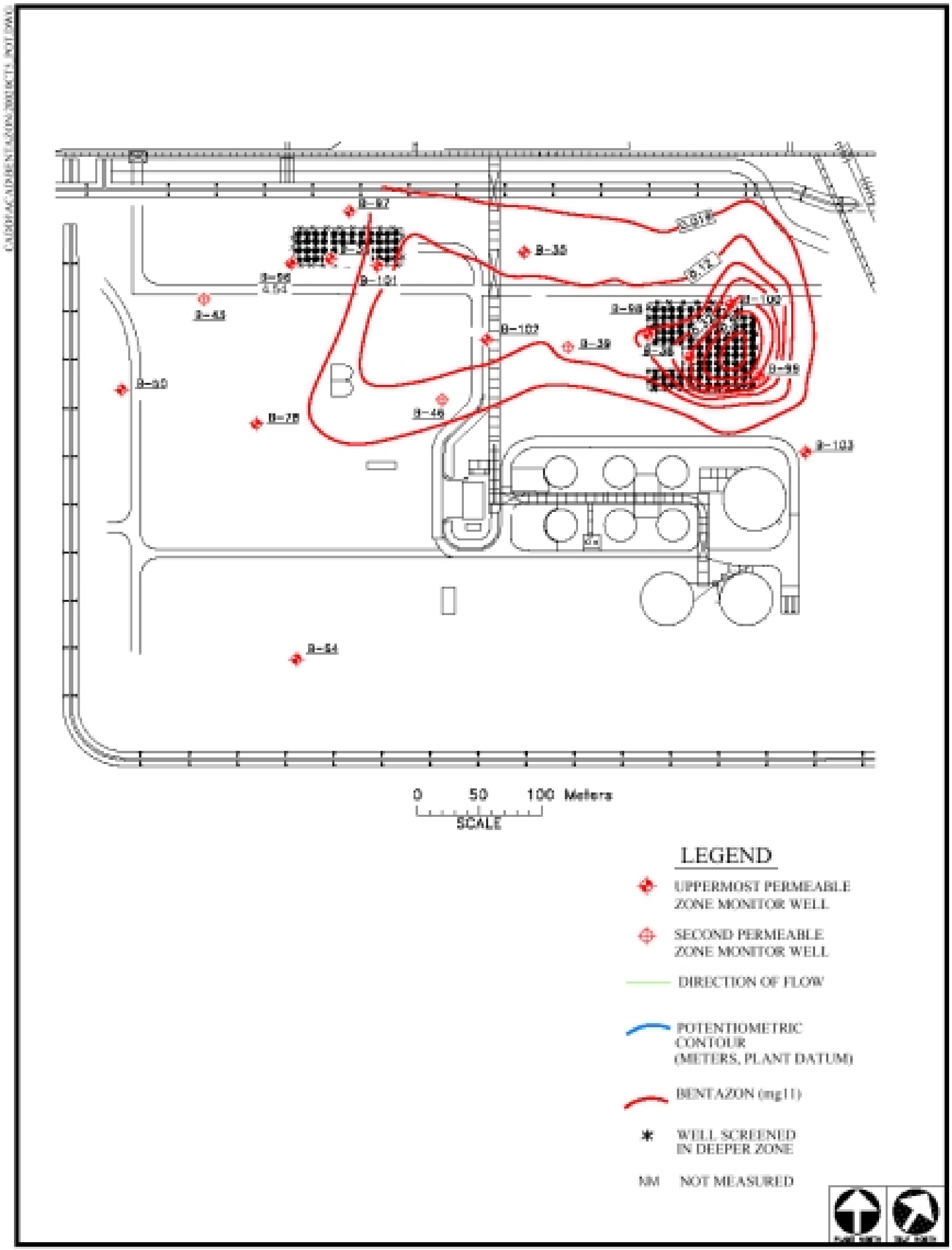


Figure 4.9: Map of the Predicted Bentazon Concentrations after 5 years of Phytoremediation

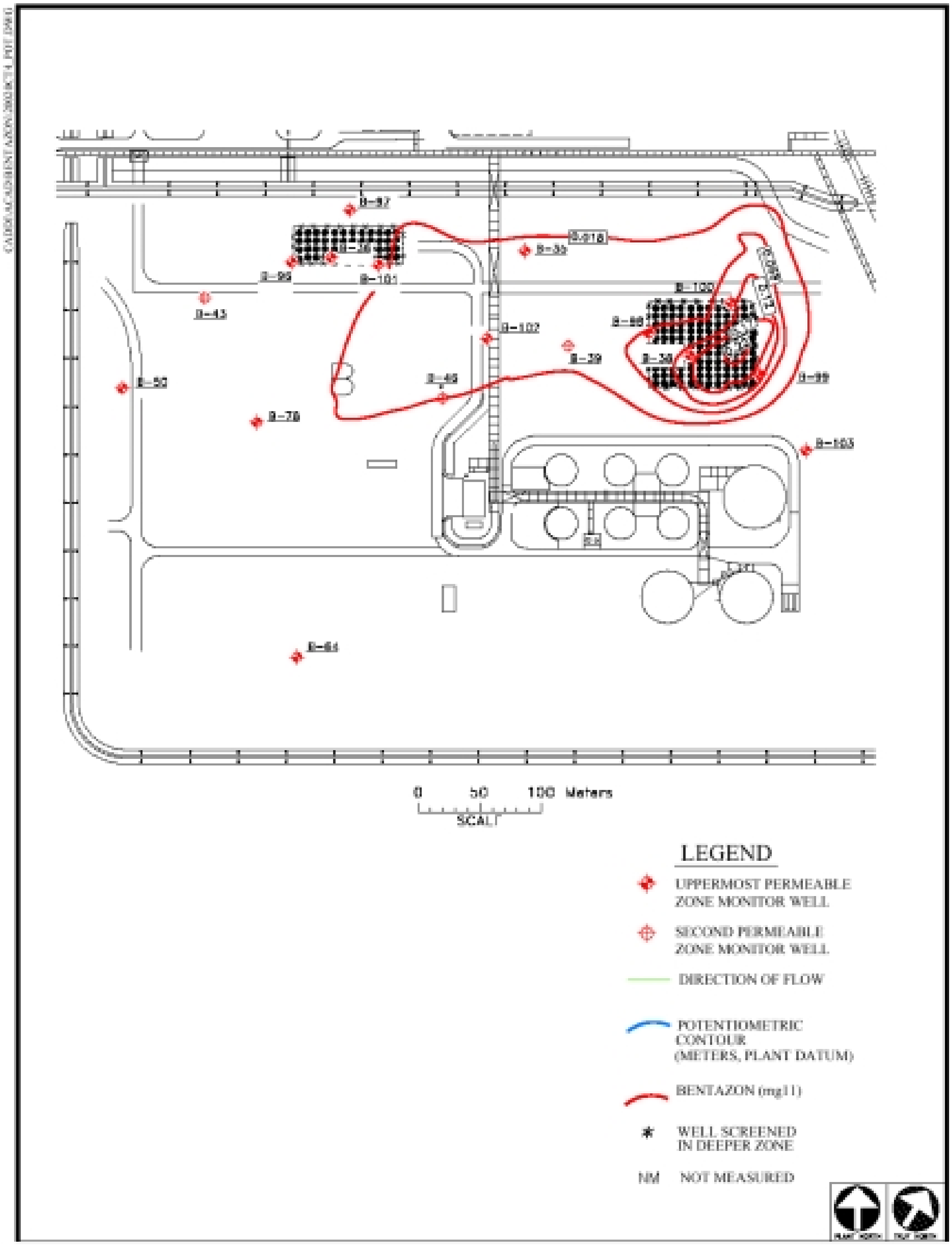


Figure 4.10: Map of the Predicted Bentazon Concentrations after 10 years of Phytoremediation

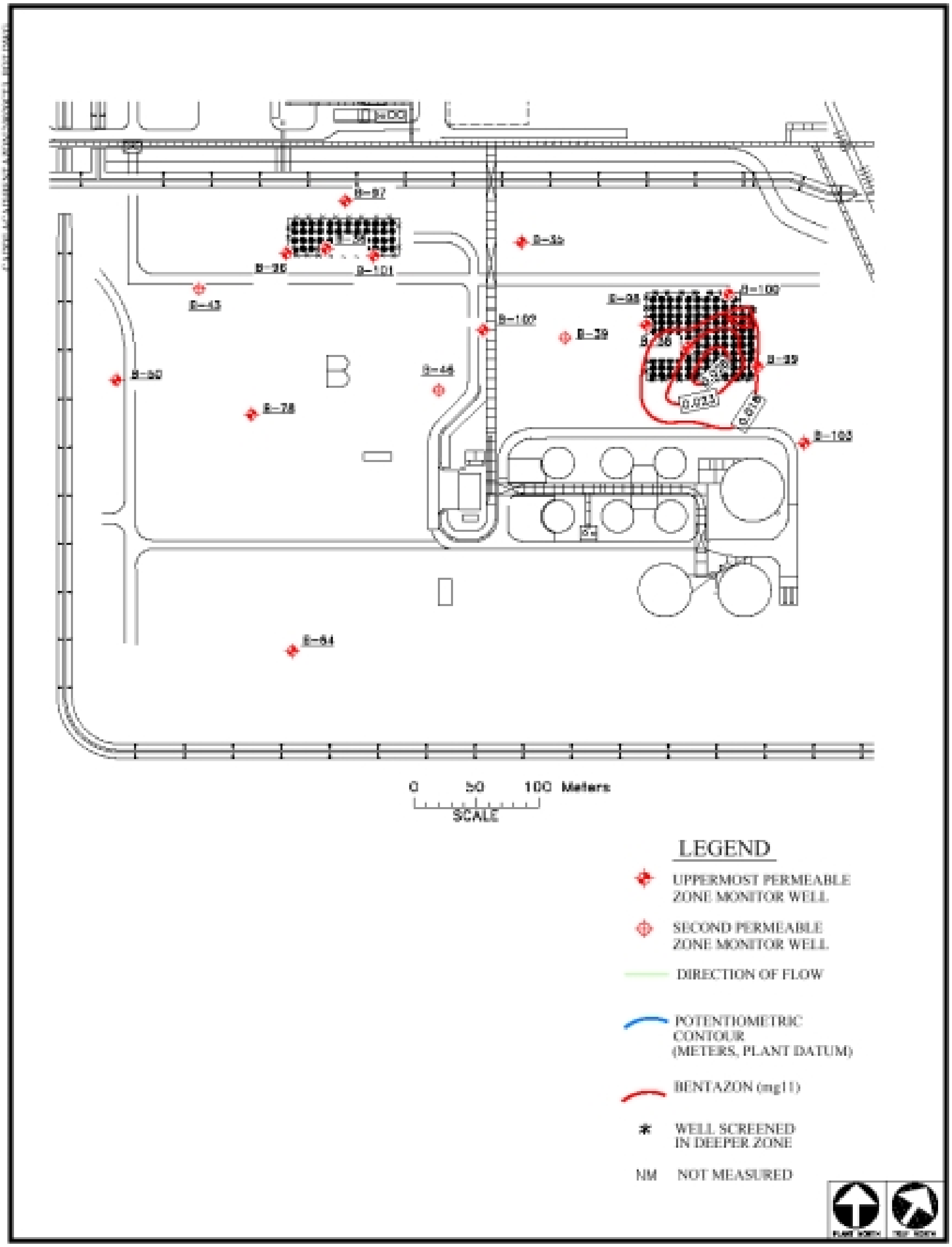


Figure 4.11: Map of the Predicted Bentazon Concentrations after 20 years of Phytoremediation

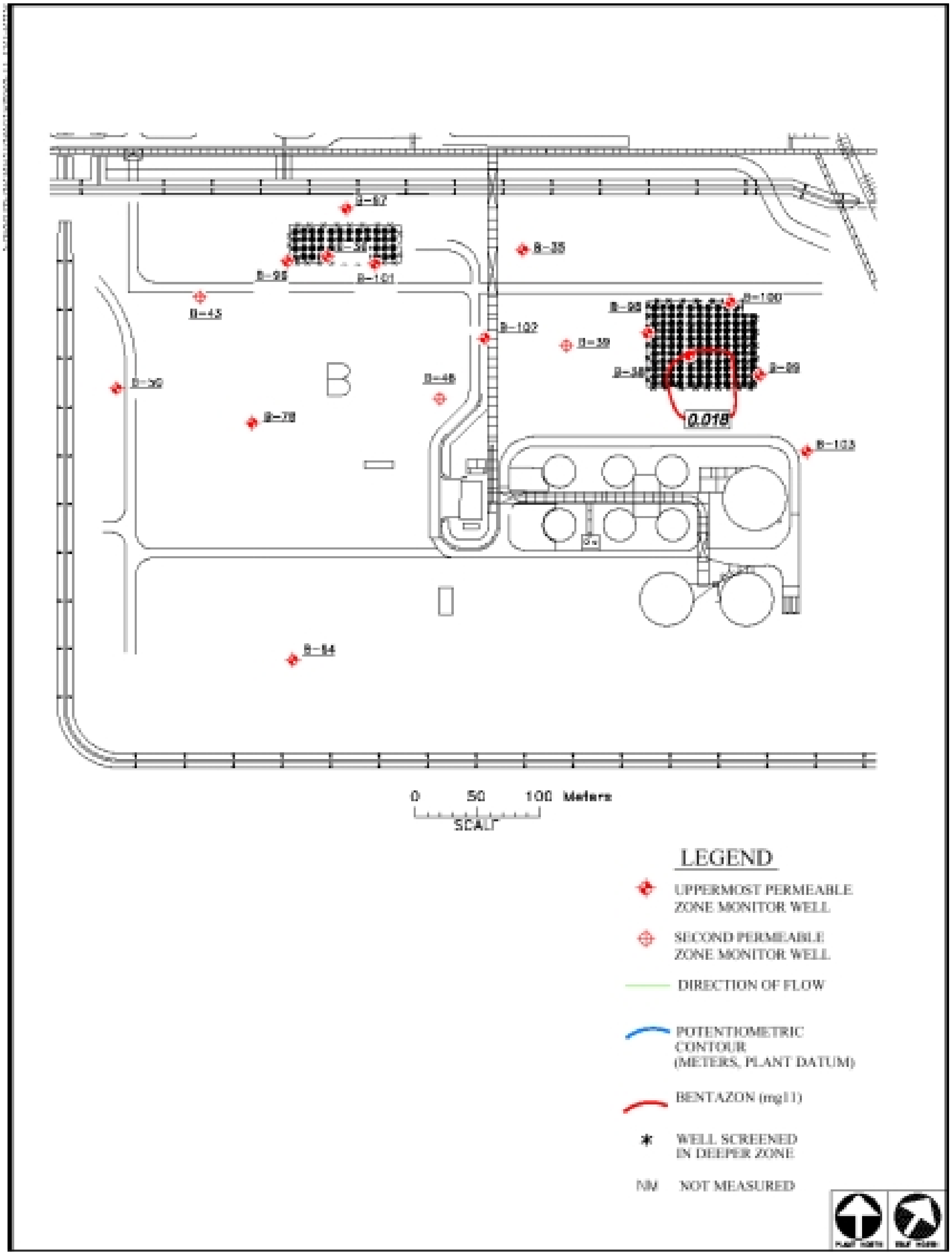


Figure 4.12: Map of Predicted Bentazon Concentrations after 22 years of Phytoremediation.

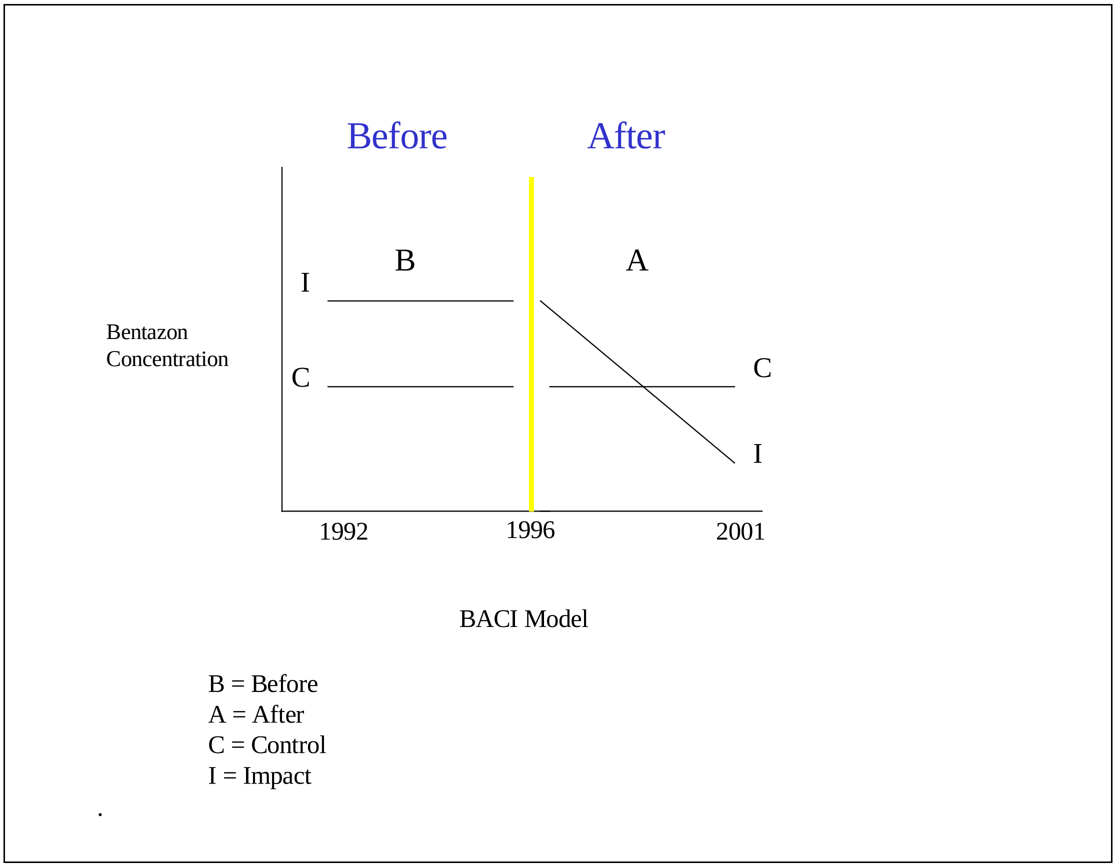


Figure 4.13: Before After Control Impact (BACI) Model (Smith, 2002)

The before phytoremediation conditions are shown by Figure 4.14, which is the July 1996 isoconcentration map of the bentazon concentrations in the shallow groundwater in the test area. These maps were hand-drawn using the point interpolation method. This map depicts an oblong plume of bentazon concentrations ranging from low ug/l concentrations to as great as 3 mg/l. After phytoremediation began in October 1996, monthly monitoring was conducted through March 2001 at each test plot. The after phytoremediation conditions are illustrated by Figure 4.15, which depicts the bentazon isoconcentration map after five years of phytoremediation in February 2001. It shows concentrations below 2 mg/l, suggesting that there may be a decrease in bentazon concentrations. Therefore, an initial hypothesis was that the overall bentazon concentration decreased between 1996 to 2001 compared to those observed prior to October 1996 as a result of phytoremediation.

To further examine this hypothesis and to evaluate it on an individual well basis, line graphs of each of the four wells being monitored monthly at both plots were plotted. A regression fit of the plotted trendline before phytoremediation for the bentazon concentration is illustrated by Figure 4.16 for Well B-36 at Plot 1. This graph suggests that the bentazon concentration was slightly increasing prior to 1996, but the after phytoremediation bentazon concentrations appear to decrease after 1996 (Figure 4.17). The r^2 values for each of these line graphs indicate the relative fit of the trend line to the data sets. Figures 4.18, 4.19, and 4.20 depict the after data set for Wells B-96, B-97, and B-101 at Plot 1 and show a similar decreasing trend.

At Plot 2, Well B-38 was plotted with its before and after data sets, which are shown in Figures 4.21 and 4.22. The regression fitted line of the before set suggests a slight increase in the trend of bentazon concentration from 1992 to 1996. However, the regression fitted line of the after set suggests that bentazon concentrations began decreasing after October 1996. Wells B-98, B-99, and B-100 from Plot 2 have line graphs of the after data set plotted in Figures 4.23, 4.24, and 4.25. Regression fitted trend lines of the data also suggest bentazon concentrations decreased at Plot 2 after 1996.

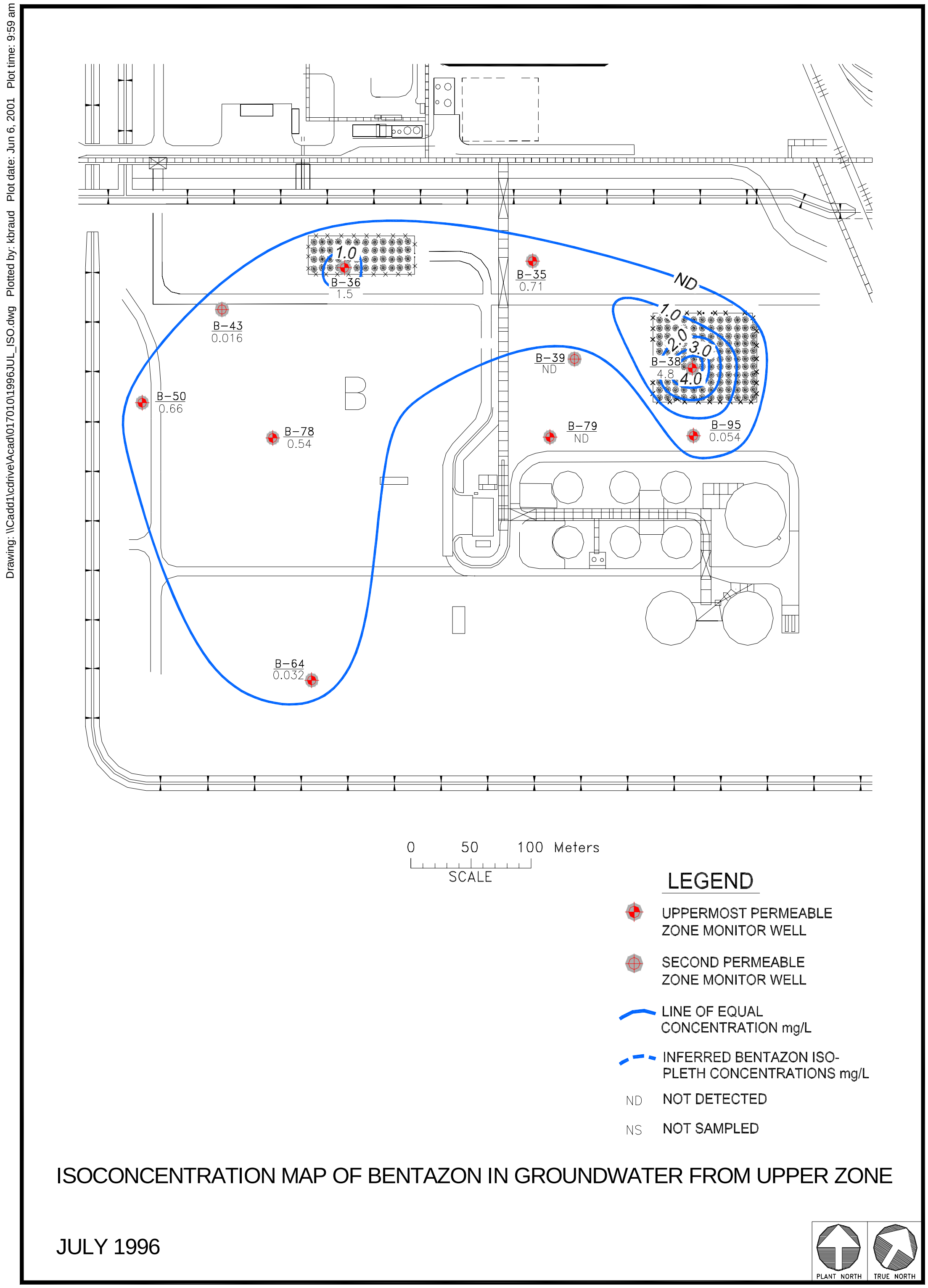


Figure 4.14: Bentazon Isoconcentration Map July 1996 at Test Site

Drawing: \\Cadd1\cdrive\Acad\017010\2001FEB_ISO.dwg Plotted by: kbraud Plot date: Jun 6, 2001 Plot time: 10:11 am

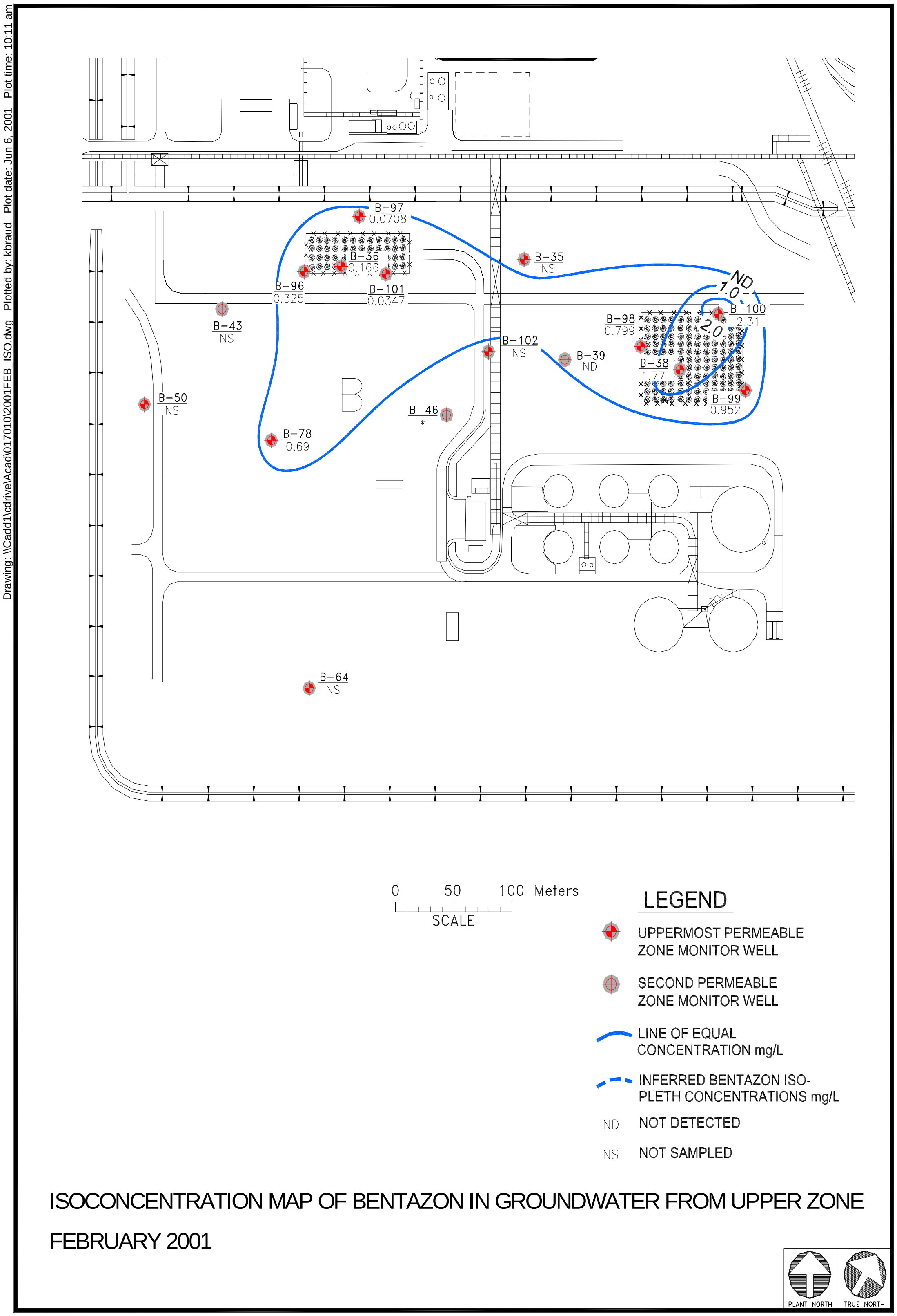


Figure 4.15. Bentazon Isoconcentration Map of February 2001 at Test Site

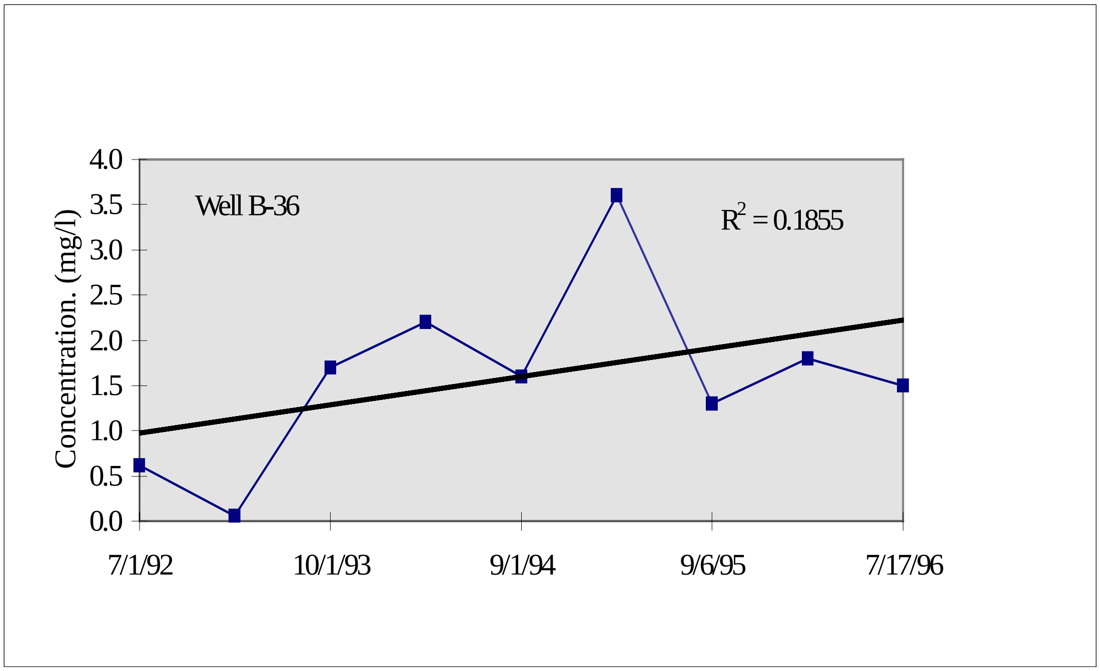


Figure 4.16: Before Phytoremediation Bentazon Concentrations in Well B-36, Plot 1

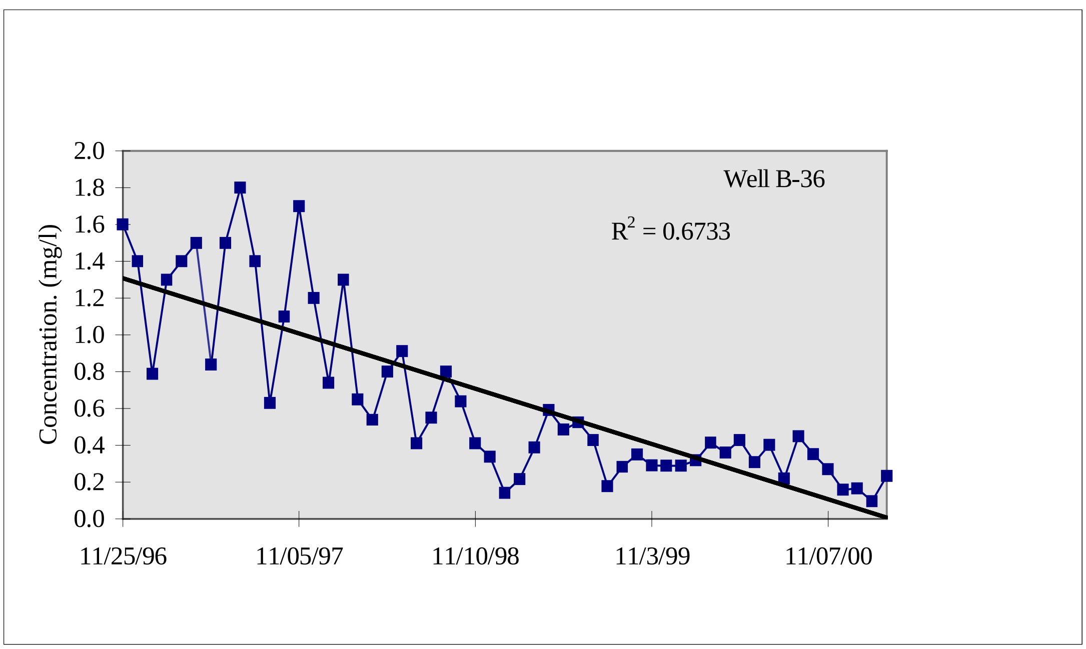


Figure 4.17: After Phytoremediation Bentazon Concentrations in Well B-36, Plot 1

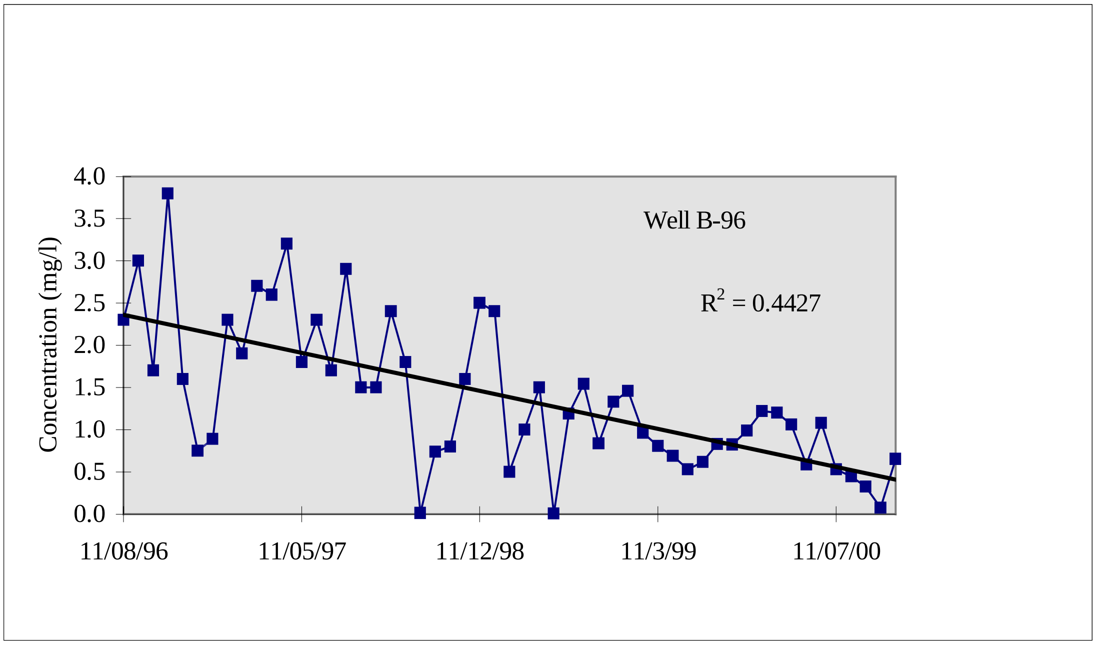


Figure 4.18: After Phytoremediation Bentazon Concentrations in Well B-96, Plot 1

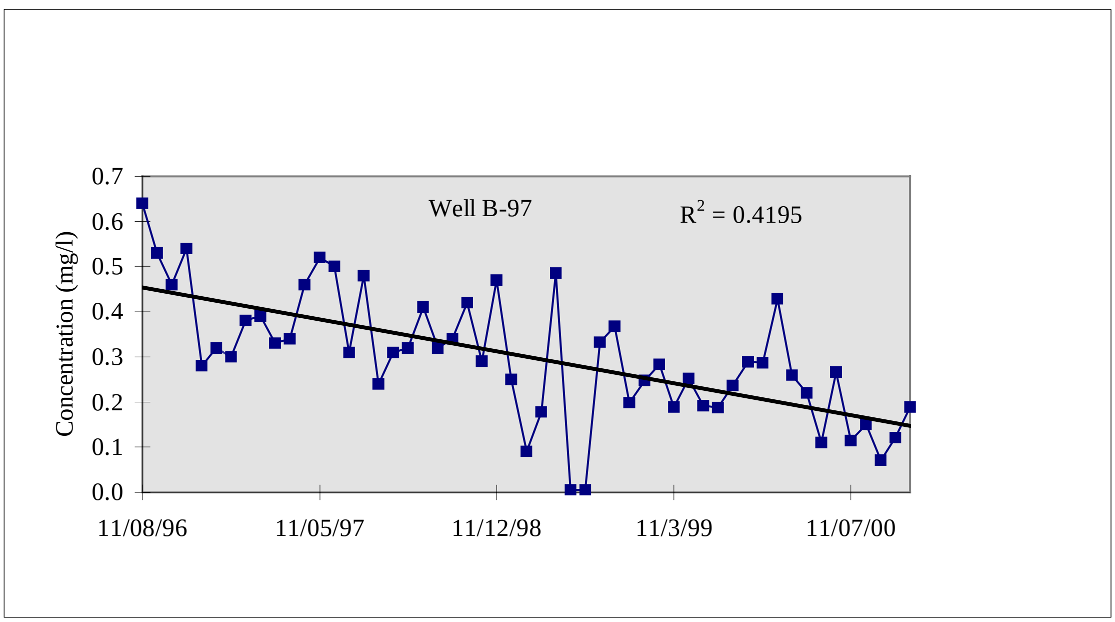


Figure 4.19: After Phytoremediation Bentazon Concentrations in Well B-97, Plot 1

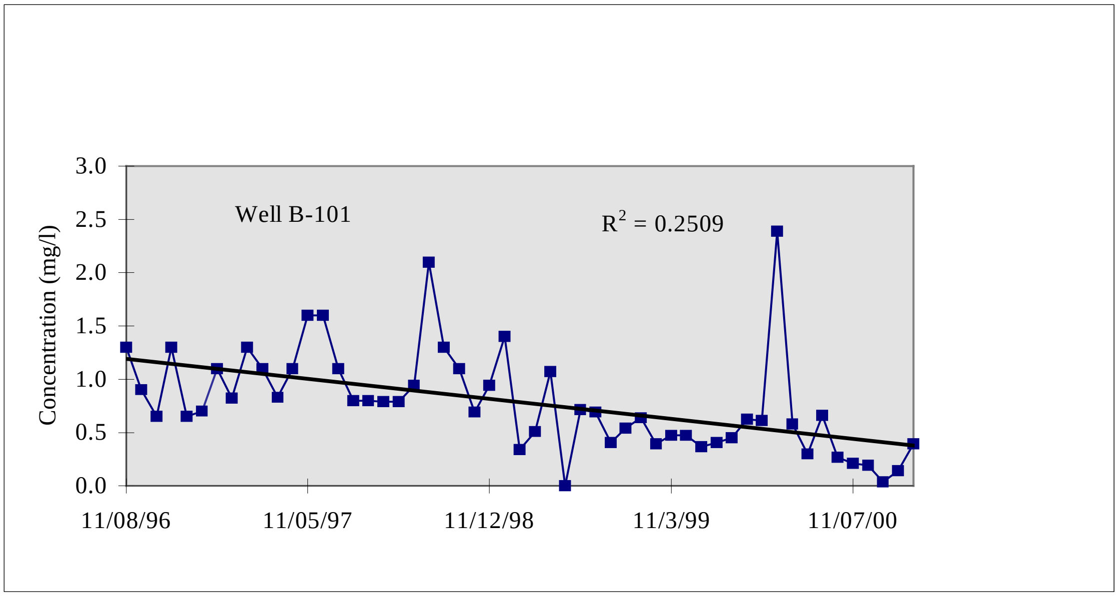


Figure 4.20: After Phytoremediation Bentazon Concentrations in Well B-101, Plot 1

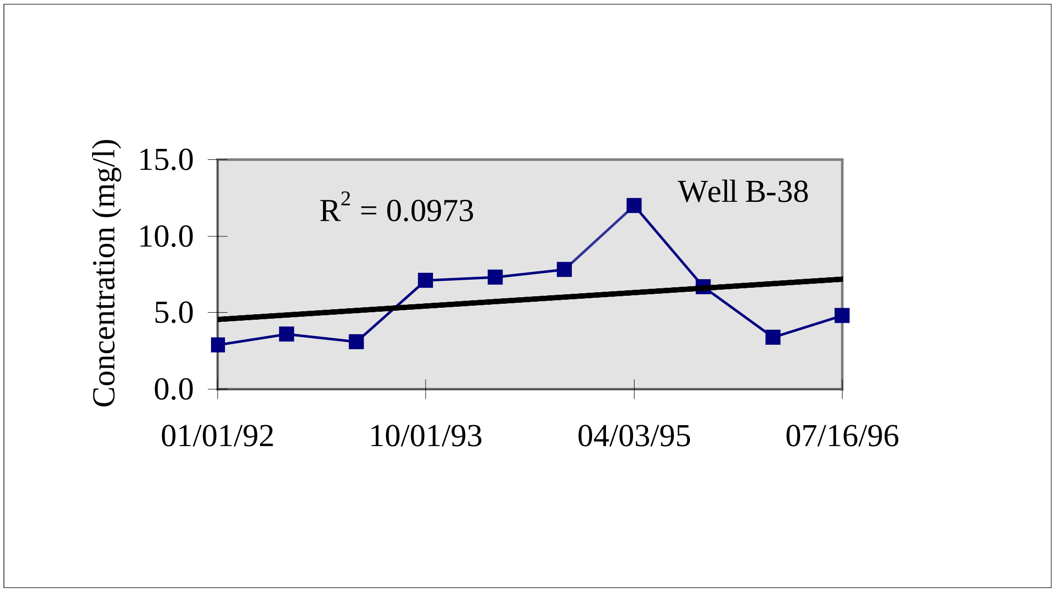


Figure 4.21: Before Phytoremediation Bentazon Concentrations in Well B-38, Plot 2

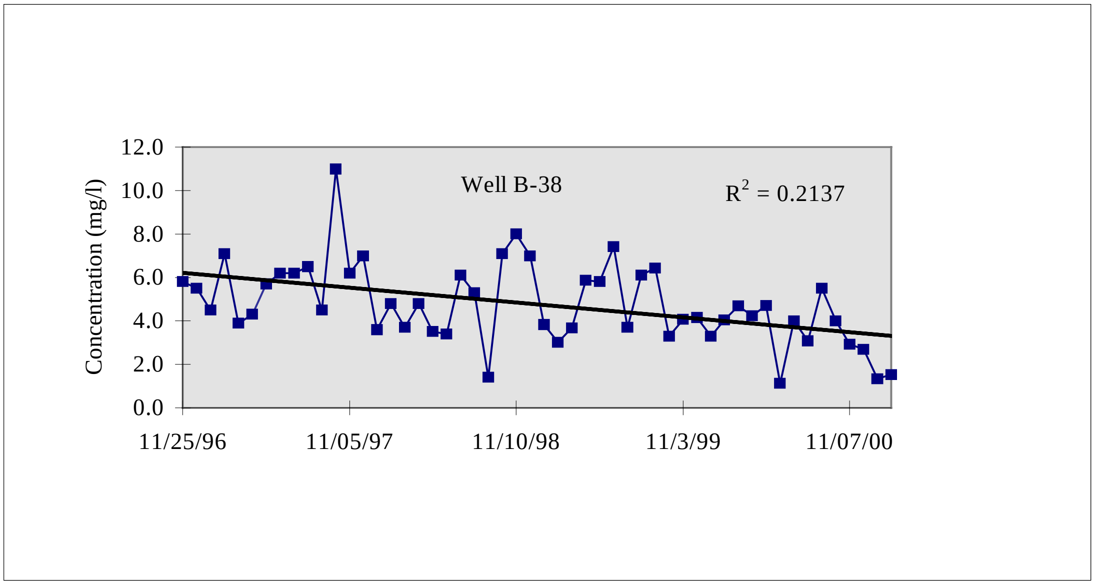


Figure 4.22 After Phytoremediation Bentazon Concentrations in Well B-38, Plot 2

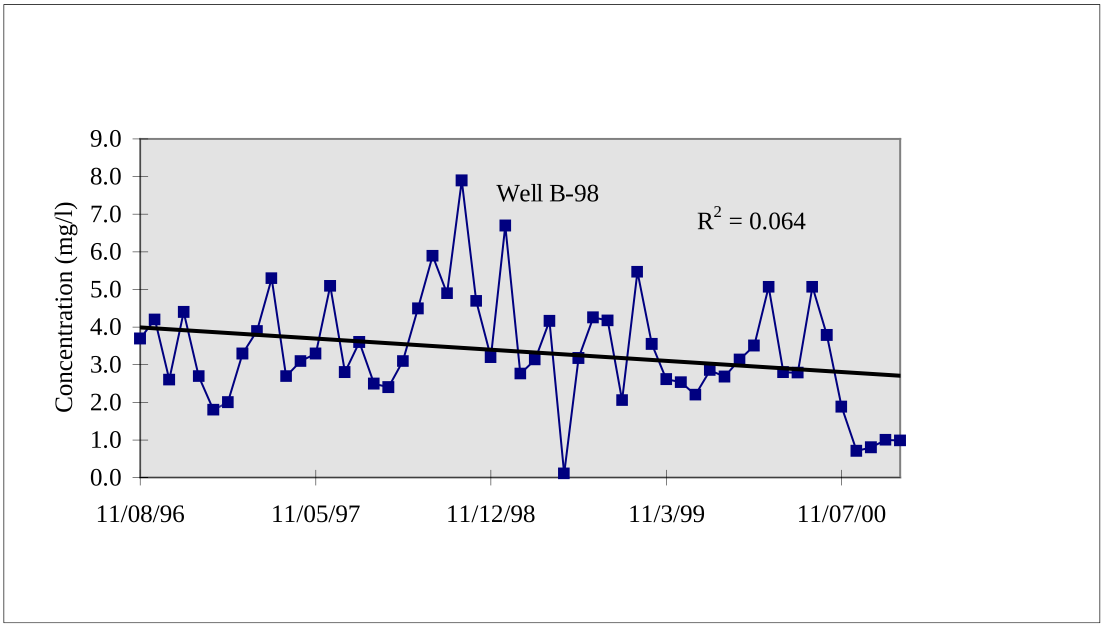


Figure 4.23: After Phytoremediation Bentazon Concentrations in Well B-98, Plot 2

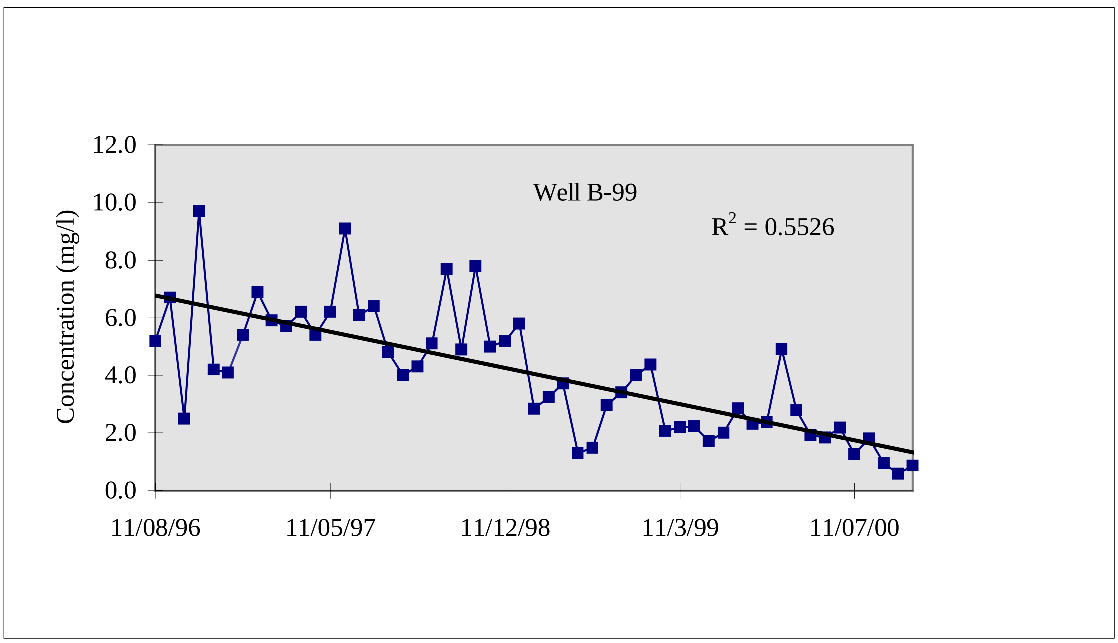


Figure 4.24: After Phytoremediation Bentazon Concentrations in Well B-99, Plot 2

Consideration should also be given to the control set of wells to determine if it can be hypothesized that these observed trends are unique to the phytoremediation plots themselves, or are the observed trends occurring outside the phytoremediation as well. If the later were possible, then it would be conceivable that some other factor could be related to the decreasing trends in bentazon concentration other than phytoremediation.

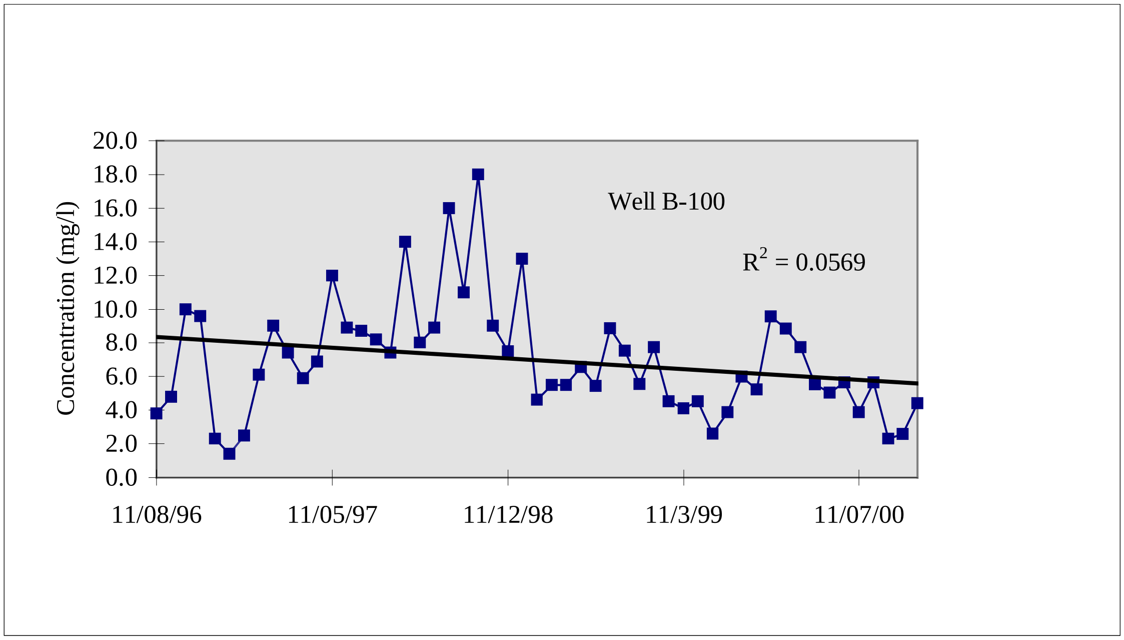


Figure 4.25: After Phytoremediation Bentazon Concentrations in Well B-100, Plot 2

To investigate these hypotheses, the control data sets were line graphed and plotted with regression trend lines. At Plot 1 the control well was B-78, which was located approximately 100 meters southeast of Plot 1. The well is outside the area of influence of the phytoremediation treatment and contains low levels of bentazon. As depicted in Figure 4.26, the regression fitted line of the bentazon concentrations in this well suggest that the data are relatively stable and have only slightly increased since 2001. In Plot 2, Well B-35 served as the control well, which was located approximately 100 meters west of the plot. The graphed data from Well B-35 is shown in Figure 4.27 indicating a similar result to Plot 1, that the bentazon concentration is not changing, but stable.

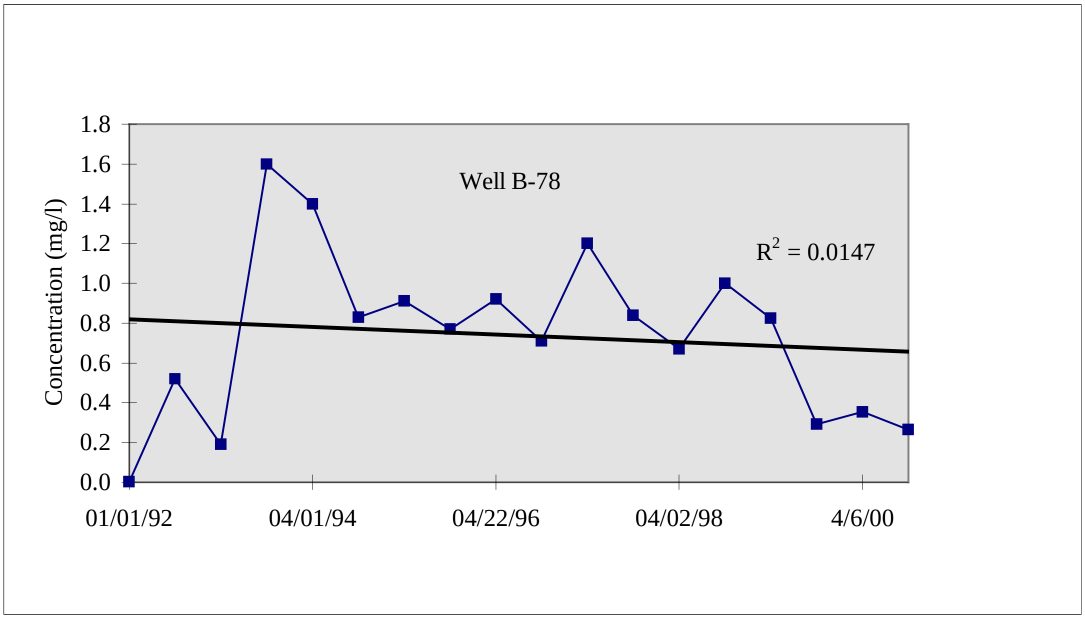


Figure 4.26: Control Data Set Well B-78, Plot 1

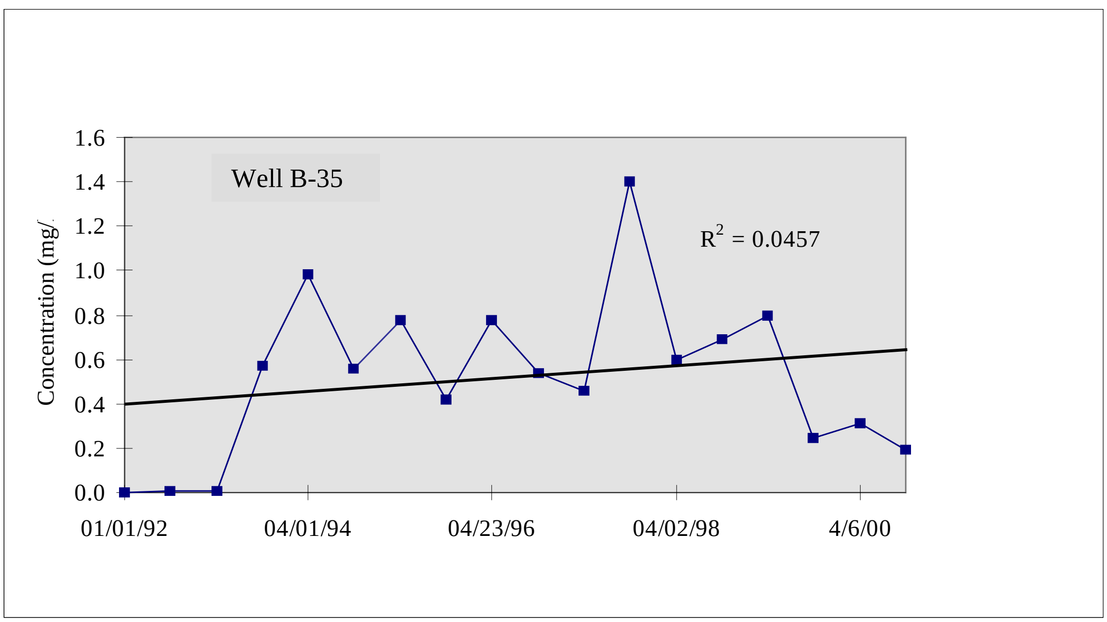


Figure 4.27: Control Data Set Well B-35, Plot 2

In summary, several hypotheses can be made. First, both spatially mapped and graphically plotted data suggest that a decreasing trend may exist in bentazon concentrations within both Plot 1 and Plot 2 between 1996 to 2001. Second, phytoremediation may be the direct causal relationship for these trends since unaffected, control areas do not appear to show any change in bentazon concentrations from 1992 to 2001. To evaluate whether these observed trends are statistically significant, the BACI model would require statistical testing. If the statistical testing of the BACI model supports the validity of these hypotheses, the objective of determining that black willow phytoremediation was effective at removing bentazon from the shallow groundwater could be substantiated.

4.5 Statistical Modeling of Bentazon Concentration Before and After Phytoremediation

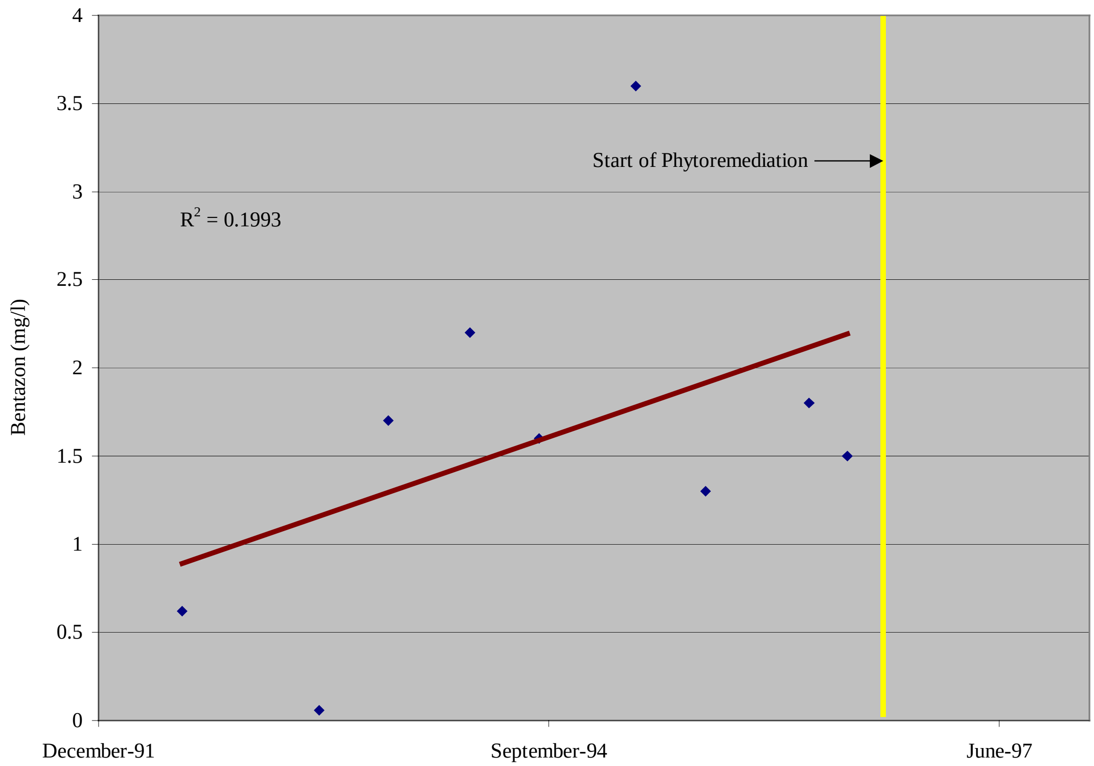
The final objective of this research study was to evaluate the effectiveness of the phytoremediation plots at reducing the bentazon concentration in shallow groundwater. As depicted graphically in the preceding section, there are several hypotheses that can be formulated concerning the bentazon concentration in groundwater. The first hypothesis tested the assertion that bentazon concentrations decreased in the within both Plot 1 and Plot 2 between 1996 to 2001. The second hypothesis tested whether phytoremediation was responsible for the bentazon concentrations observed in the groundwater or some other environmental factor. Validation of these hypotheses accomplished the final research study objective, to evaluate the effectiveness of black willow phytoremediation to remove bentazon from shallow groundwater.

The BACI Model previously described was used as the design basis to test the first hypothesis. An analysis of variance (ANOVA) test was used to test the whether the means of the bentazon concentrations before phytoremediation against those after phytoremediation began for equality. This was the null hypothesis of the ANOVA test. The statistic used to evaluate the significance of the means by ANOVA was a standardized Student's T Test. As described by the BACI model, datasets were arranged into three treatments, a Plot 1 impact treatment, a Plot 2 impact treatment, and a control treatment. The impact treatments each included before and after phytoremediation datasets as did the control treatment. The historical bentazon concentrations from each of the four groundwater monitoring wells at each plot made up the impact treatment data sets. Four wells where chosen outside the hydraulic influence of the phytoremediation plots, the closest being over 100 meters away, as the control treatment.

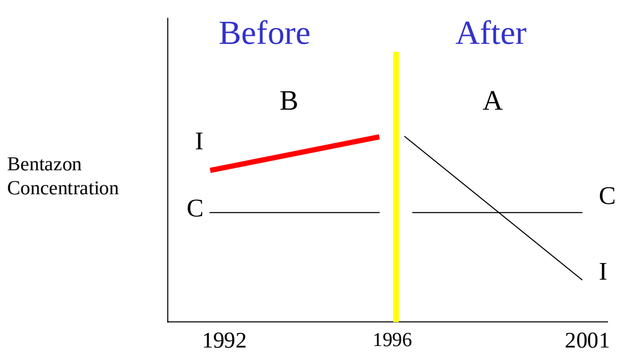
Table 4.3 contains the tabulated summary statistics for each of the data sets of the BACI Model for Plot 1, Plot 2 and the Control treatments. As shown, the mean bentazon concentration did decrease before phytoremediation as compared to after phytoremediation in the Plot 1 and Plot 2 treatments, while the mean bentazon concentration of the control treatment was slightly increased during the same period. These data are illustrated by Figures 4.28, 4.29, 4.30, 4.31 and 4.32 as they relate to the BACI Model. The best fit regression trend line and the corresponding r^2 value are depicted for each data set. To complete the ANOVA test for the first hypothesis, the standardized Student T Test was performed on the data sets. The results tabulated in Table 4.4 indicate that the decrease in mean bentazon concentration observed in the Plot 1 Impact treatment from before to after phytoremediation is significant with the probability equal to 0.02. However, in the case of the Plot 2 Impact treatment, while a decrease is observed in the bentazon concentration mean from before to after phytoremediation, the means are not significantly different, since the probability is equal to 0.09, thus invalidating the test of the null hypothesis. However, even though this test does not indicate significance within a probability of 0.05, it does provide some evidence suggesting that the mean bentazon concentration decreased in the Plot 2 Impact treatment. The Student's T test of the control treatment indicates no significant increase in the bentazon concentration mean with probability of 0.23. This would be expected in the Control Treatment of a BACI Model. Therefore, the first hypothesis, that bentazon concentrations in groundwater decreased after phytoremediation began can be supported for Plot 1 and some evidence suggests that bentazon concentration may have decreased in Plot 2 after phytoremediation.

Table 4.3: Summary Statistics for the BACI Model of Bentazon Concentrations at the Phytoremediation Test Site

PLOT 1 BEFORE		PLOT 1 AFTER	
Mean	1.5975	Mean	0.7824
Standard Error	0.3302	Standard Error	0.0465
Standard Deviation	0.9905	Standard Deviation	0.6767
Sample Variance	0.9810	Sample Variance	0.4579
Minimum	0.058	Minimum	0.0005
Maximum	3.6	Maximum	3.8
Sum	14.378	Sum	165.859
Number of Samples	9	Number of Samples	212
Confidence Level (95.0%)	1.5975 ±0.7613	Confidence Level (95.0%)	0.7824 ±0.0916
PLOT 2 BEFORE		PLOT 2 AFTER	
Mean	6.2	Mean	4.7829
Standard Error	0.9475	Standard Error	0.1863
Standard Deviation	2.8425	Standard Deviation	2.7057
Sample Variance	8.08	Sample Variance	7.3209
Minimum	3.1	Minimum	0.103
Maximum	12	Maximum	18
Sum	55.8	Sum	1009.183
Number of Samples	9	Number of Samples	211
Confidence Level (95.0%)	6.2 ±2.185	Confidence Level (95.0%)	4.7829 ±0.3672
CONTROL BEFORE		CONTROL AFTER	
Mean	0.3563	Mean	0.4236
Standard Error	0.0637	Standard Error	0.0667
Standard Deviation	0.4272	Standard Deviation	0.3773
Sample Variance	0.1825	Sample Variance	0.1424
Minimum	0	Minimum	0.001
Maximum	1.6	Maximum	1.4
Sum	16.0320	Sum	13.5561
Number of Samples	45	Number of Samples	32
Confidence Level (95.0%)	0.3563 ±0.1283	Confidence Level (95.0%)	0.4236 ±0.1360



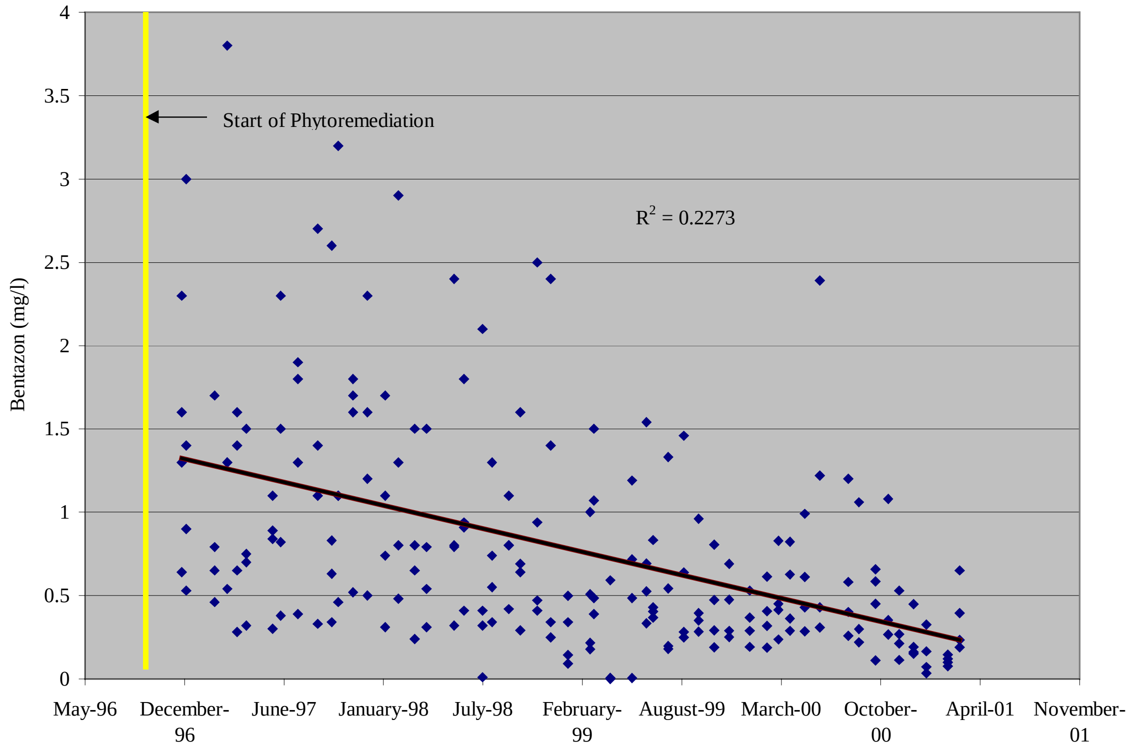
Model Key to Graph



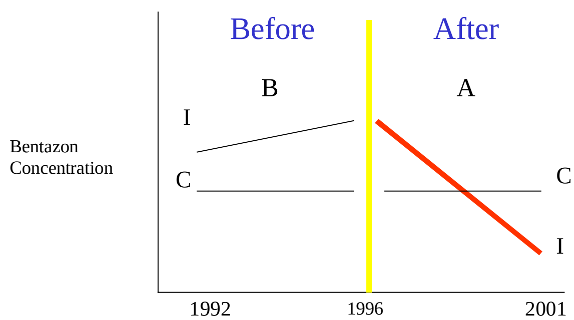
BACI Model

B=Before
A=After
C=Control
I=Impact

Figure 4.28: Plot 1 Impact Treatment, Before Phytoremediation Data Set of Bentazon Groundwater Concentrations



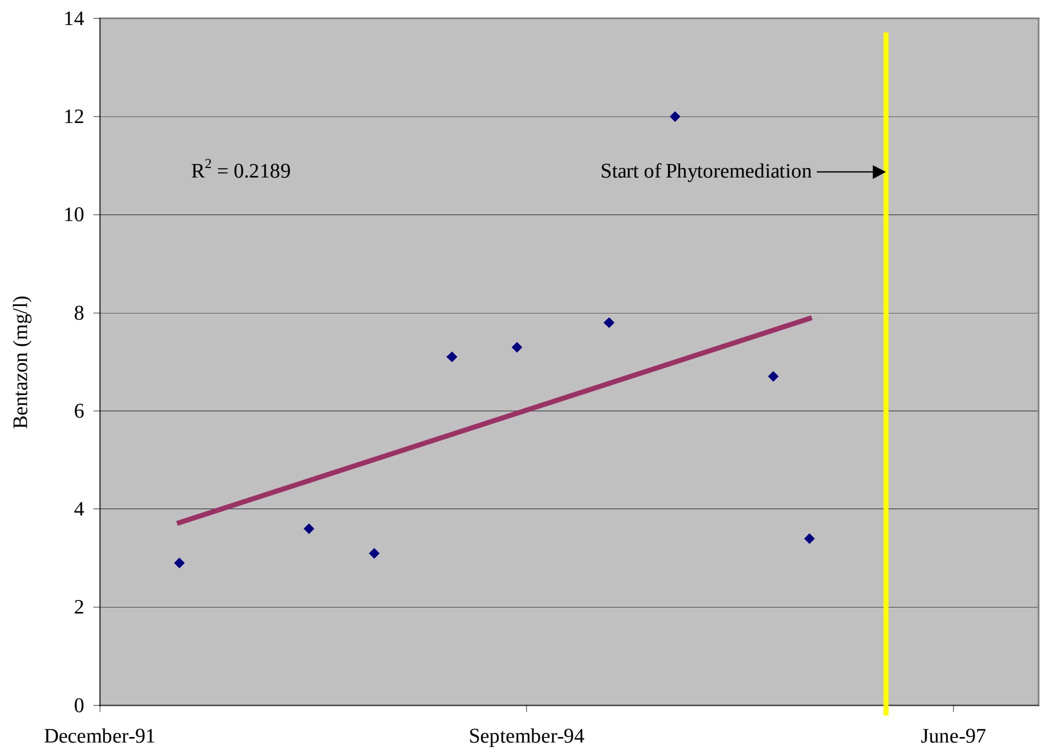
Model Key to Graph



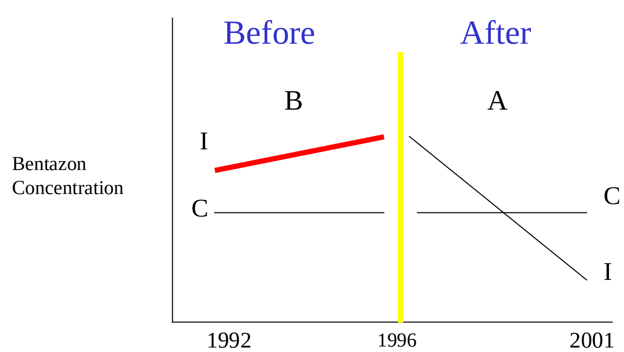
BACI Model

B=Before
A=After
C=Control
I=Impact

Figure 4.29: Plot 1 Impact Treatment, After Phytoremediation Data Set of Bentazon Groundwater Concentrations



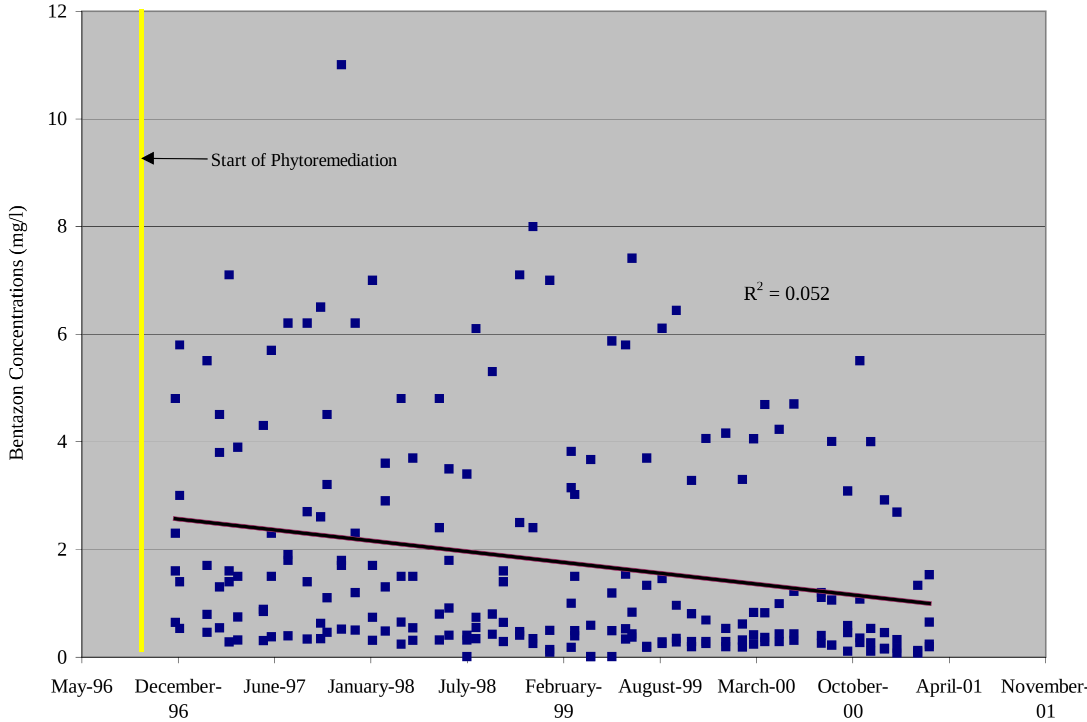
Model Key to Graph



BACI Model

B=Before
A=After
C=Control
I=Impact

Figure 4.30: Plot 2 Impact Treatment, Before Phytoremediation Data Set of Bentazon Groundwater Concentrations



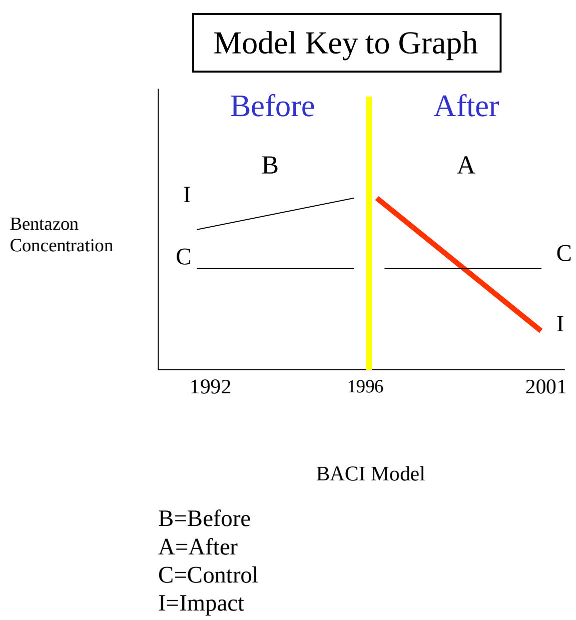
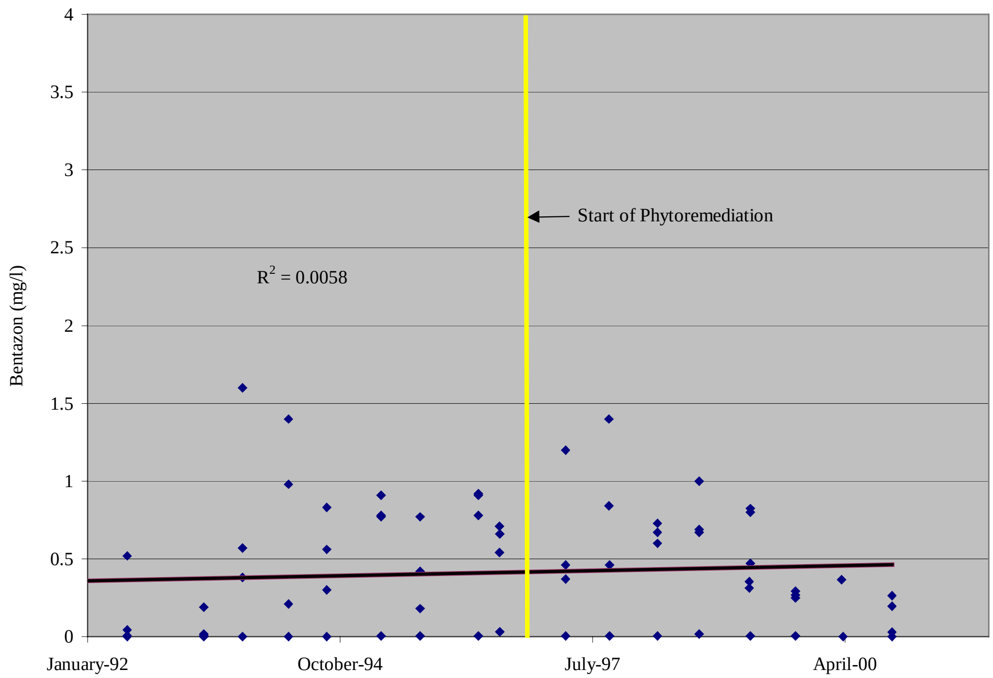
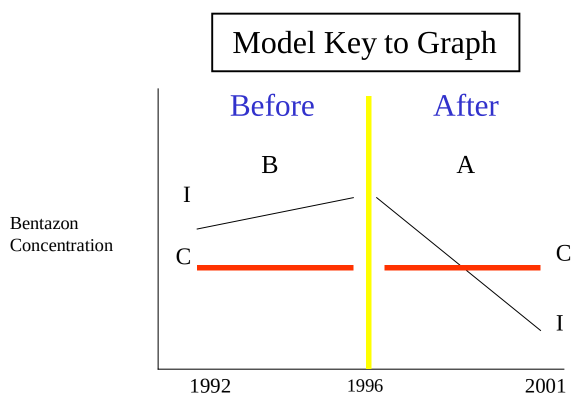


Figure 4.31: Plot 1 Impact Treatment, After Phytoremediation Data Set of Bentazon Groundwater Concentrations





BACI Model

B=Before
A=After
C=Control
I=Impact

Figure 4.32: Control Treatment, Before and After Phytoremediation Data Sets

Table 4.4: Student's T Test of Analysis of Variance for Phytoremediation Plots

t-Test: Two-Sample Assuming Unequal Variances

	PLOT 1 BEFORE	PLOT 1 AFTER
Mean	**1.597555556**	**0.782352358**
Variance	0.981013778	0.457917625
Observations	9	212
Hypothesized Mean Difference	0	
Degrees of Freedom	8	
t Statistic	2.445055022	
P(T≤t) one-tail	**0.020122965**	
t Critical one-tail	1.85954832	

	PLOT 2 BEFORE	PLOT 2 AFTER
Mean	**6.2**	**4.78285782**
Variance	8.08	7.320897875
Observations	9	211
Hypothesized Mean Difference	0	
Degrees of Freedom	9	
t Statistic	1.467557292	
P(T≤t) one-tail	**0.088140579**	
t Critical one-tail	1.833113856	

	CONTROL BEFORE	CONTROL AFTER
Mean	**0.356265556**	**0.423628125**
Variance	0.182499127	0.142374929
Observations	45	32
Hypothesized Mean Difference	0	
Degrees of Freedom	71	
t Statistic	-0.73044547	
P(T≤t) one-tail	**0.23376071**	
t Critical one-tail	1.666599019	

To strengthen the support for the first hypothesis and to examine the second hypothesis, that phytoremediation is the direct causal relationship for the decrease in means, Bayesian analysis was also used. Dynamic Linear Modeling (DLM) (Pole et al.,

1994) was used to evaluate the time series of bentazon concentrations and perform regression analysis of bentazon concentration as a response variable to other environmental factors such as water level, rainfall, or river stage. In this statistical analysis, DLMs were assembled for the impact treatment using Well B-36 for Plot 1 and Well B-38 for Plot 2. The control treatments were Well B-78 for Plot 1 and Well B-35 for Plot 2. These wells were chosen from the control group because, while out of the area of influence of phytoremediation, they were closer to the respective Plot they were chosen to represent. This method improved the ability to determine the outcome of a model that the response variable is constantly responding in time in a series as treatment progresses (Pole et al., 1994). Seasonality and possible relationships with river stage, groundwater level, and rainfall were also tested by DLM regression analysis. The DLM tests using the BACI design used in this study are summarized by Table 4.5.

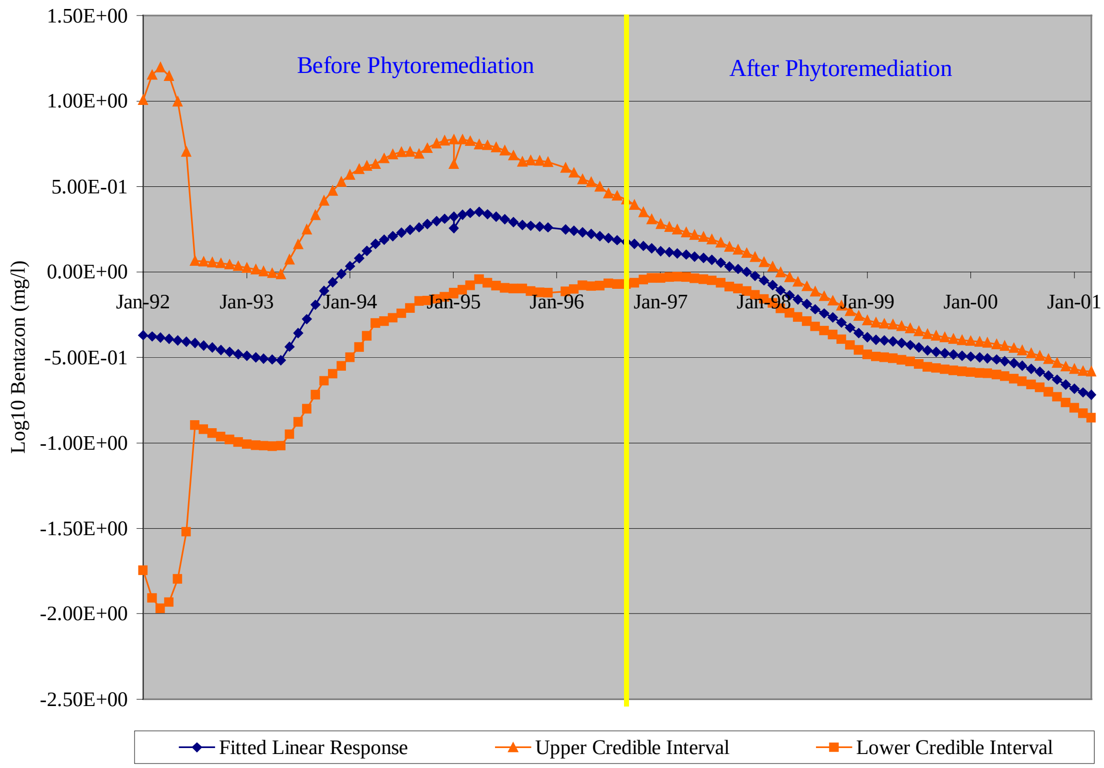
Table 4.5: DLM Testing of the Before After Control Impact Model

Treatment Plot 1	Treatment Plot 2	Tests Performed
Well B-36 (Impact Well)	Well B-38 (Impact Well)	Constant, Linear, 1st Harmonic, Seasonal Factor
Well B-78 (Control Well)	Well B-35 (Control Well)	Constant, Linear, 1st Harmonic, Seasonal Factor
Well B-36 (Impact Well)	Well B-38 (Impact Well)	Regression Analysis to River Stage, Groundwater Level, and Rainfall

The DLM for the Impact Wells of the Plot 1 and Plot 2 treatments are shown as plotted line graphs in Figures 4.33 and 4.34. While the best fit model for Well B-38 is constant, both line graphs illustrated for comparison are the linear trend models for each of the two treatments with the upper and lower 90% bounds of the credible intervals shown. These models were chosen as the best overall fit from the model search as tabulated in Table 4.6. The model search was made using the predictive log likelihood as the indicator of best fit. This data was modeled from the Bayesian Analysis of Time Series (BATS) software by Pole, et al.(1994). The line graphs of the Impact Wells illustrate similar trends as previously hypothesized concerning bentazon concentrations. Both illustrate an increasing trend before phytoremediation and a decreasing trend after phytoremediation.

Figures 4.35 and 4.36 are line graphs of the control wells for both Plot 1 and Plot 2. These line graphs also illustrate similar trends in the bentazon concentration to the previous control data. The model search shows increasingly more negative log likelihood for the seasonality tests and the regression evaluations, suggesting that the models are not as good a fit in these cases. Therefore, there is a lower likelihood of any relationship of well water level, rainfall, or river stage being responsible for a decrease in the bentazon concentrations in groundwater that were observed.

The DLMs indicate that bentazon concentrations decreased in both plots and that the decrease began after phytoremediation began in 1996. Further, control samples do not demonstrate that bentazon concentrations changed during the same period in control treatment wells outside the area of phytoremediation effect. Other environmental factors such as well water level, rainfall, or river stage had a minimal if any linear effect on the observed bentazon concentrations in groundwater. With the addition of the DLM analysis, the BACI Model statistically supports that phytoremediation accounted for the decreases in bentazon concentrations at the phytoremediation test site between 1996 and 2001.



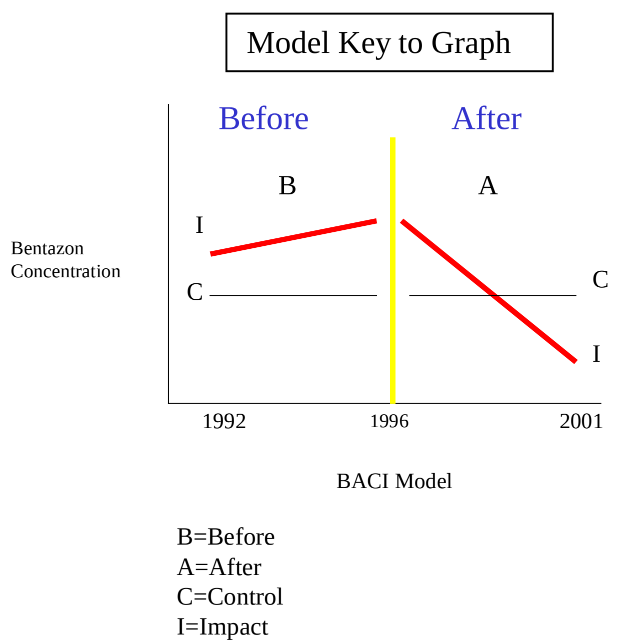
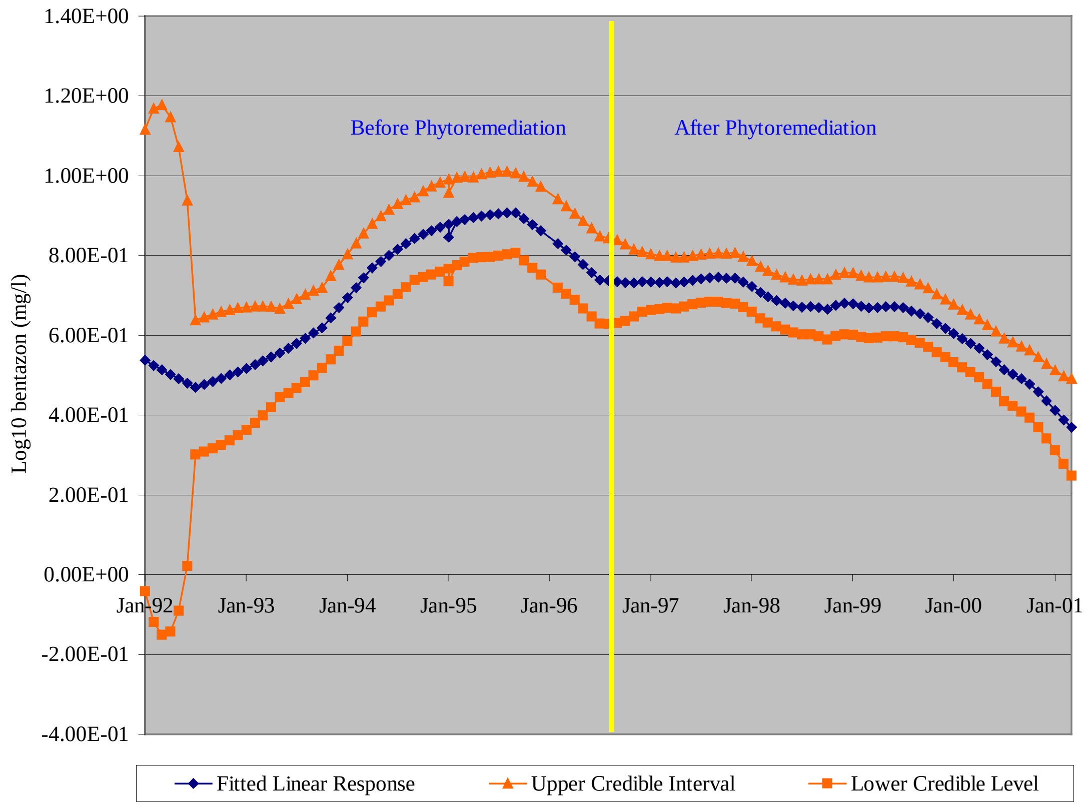


Figure 4.33: The Dynamic Linear Model of the Fitted Values, Linear Trend Model and 90% Credible Interval for Well B-36, Plot 1, the Impact Well



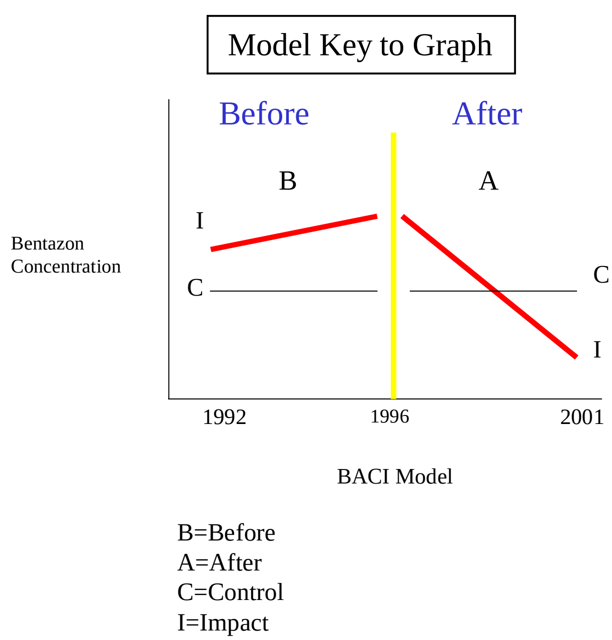
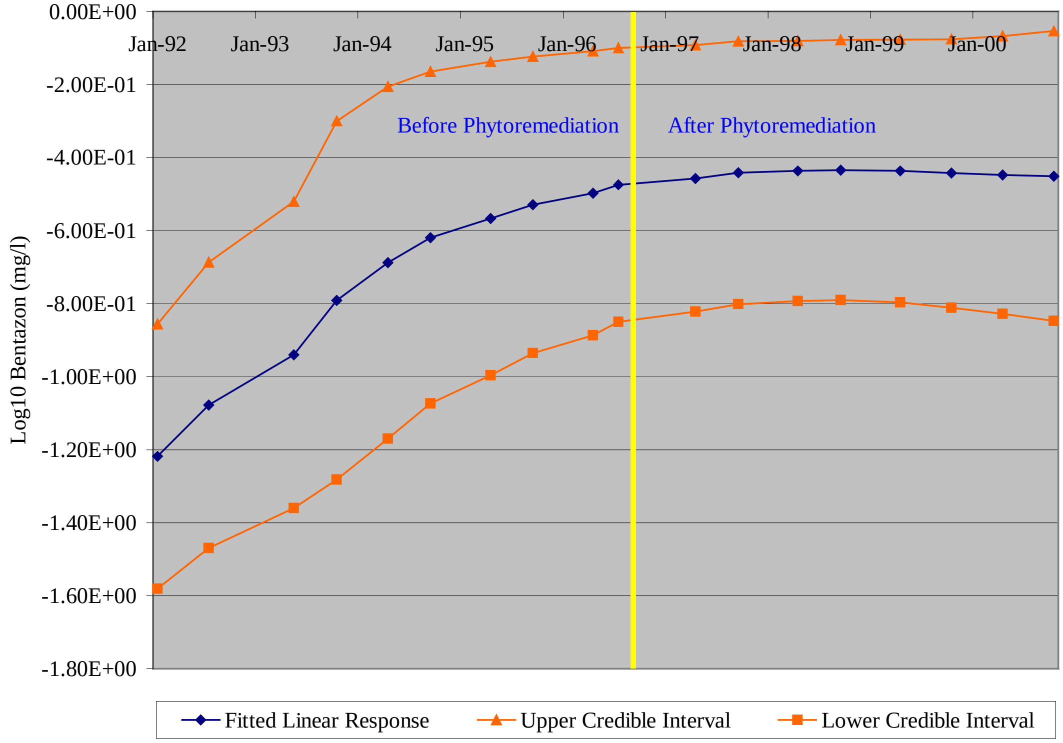
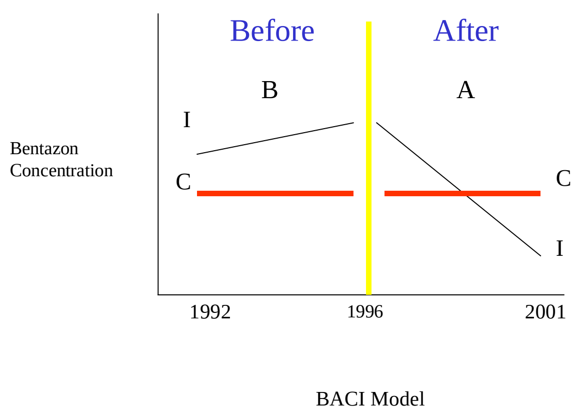


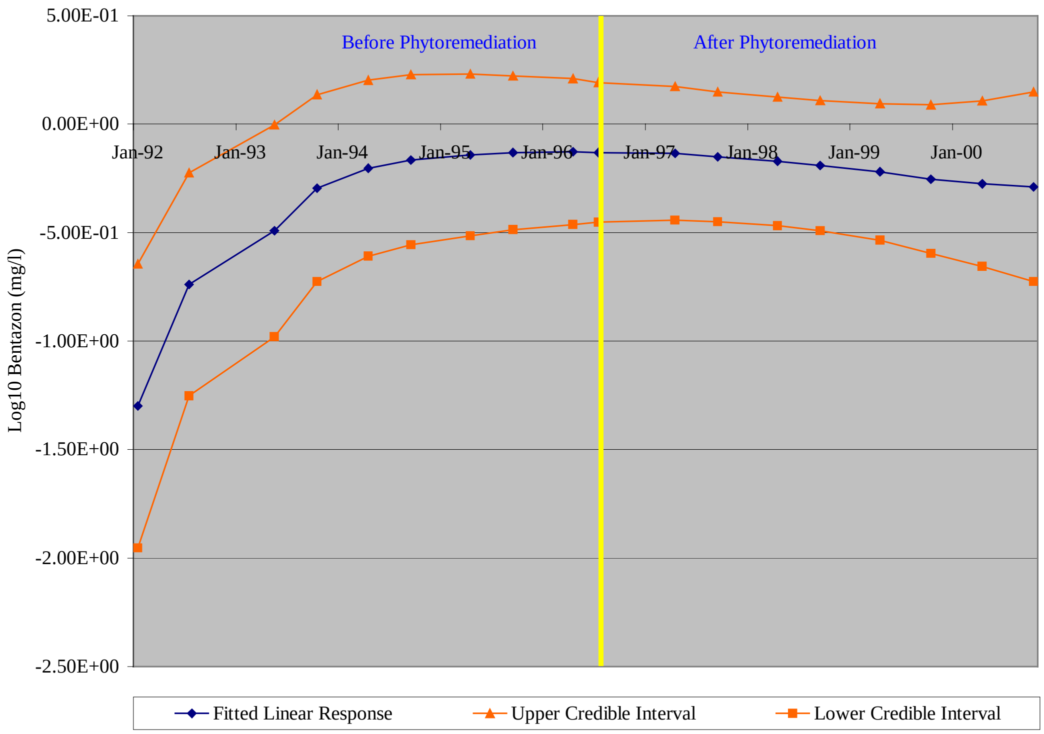
Figure 4.34: The Dynamic Linear Model of the Fitted Values, Linear Trend Model and 90% Credible Interval for Well B-38, Plot 2, Impact Well





B=Before
A=After
C=Control
I=Impact

Figure 4.35: The Dynamic Linear Model of the Fitted Values, Linear Trend Model and 90% Credible Interval for Well B-78, Plot 1, Control Well



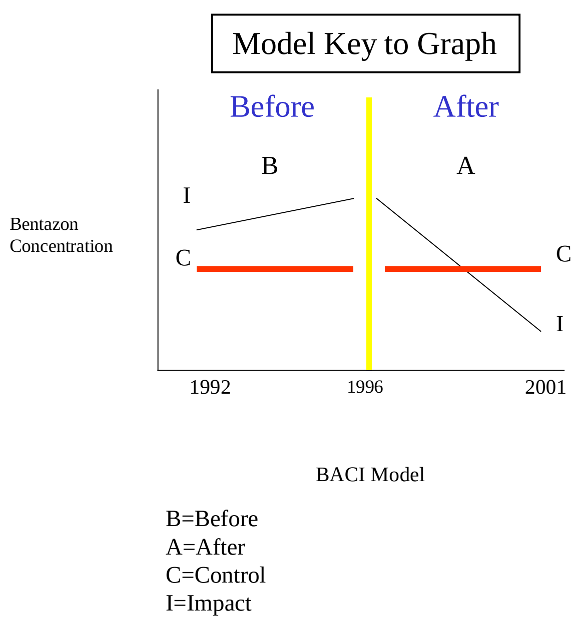


Figure 4.36: The Dynamic Linear Model of the Fitted Values, Linear Trend Model and 90% Credible Interval for Well B-35, Plot 2, Control Well

Table 4.6: Summary of Dynamic Linear Model Searches for Phytoremediation Treatments

Well	Test	Mean Squared Error	Mean Absolute Deviation	Predictive Log Likelihood
B-36 (Impact, Plot 1)	Constant	9.0916×10^{-2}	2.0181×10^{-1}	-8.6596
	Linear	8.8735×10^{-2}	1.9017×10^{-1}	-1.6931*
	Linear, 1st order Harmonic	8.7971×10^{-2}	2.1235×10^{-1}	-3.2121
	Linear, Seasonal Factor	9.3022×10^{-2}	2.0754×10^{-1}	-1.9355
	Regression with well water level	3.7155×10^{-2}	1.5647×10^{-1}	-43.325
	Regression with rainfall	9.8386×10^{-2}	2.2039×10^{-1}	-4.8537
	Regression with river stage	7.0871×10^{-2}	2.0051×10^{-1}	-4.0517
B-38 (Impact, Plot 2)	Constant	3.6097×10^{-2}	1.4472×10^{-1}	12.190*
	Linear	3.5630×10^{-2}	1.4443×10^{-1}	11.294
	Linear, 1st order Harmonic	4.8322×10^{-2}	1.7178×10^{-1}	-28.471
	Linear, Seasonal Factor	3.8075×10^{-2}	1.4975×10^{-1}	7.1143
	Regression with well water level	6.2895×10^{-2}	1.8081×10^{-1}	-32.653
	Regression with rainfall	3.9551×10^{-2}	1.4039×10^{-1}	1.8206×10^{-1}
	Regression with river stage	4.0291×10^{-2}	1.5138×10^{-1}	6.9654×10^{-1}
B-78 (Control, Plot 1)	Constant	6.2869×10^{-1}	5.8945×10^{-1}	-23.823*
	Linear	5.5340×10^{-1}	6.2502×10^{-1}	-23.985
	Linear, 1st order Harmonic	6.0429×10^{-1}	6.6733×10^{-1}	-25.104
	Linear, Seasonal Factor	6.0429×10^{-1}	6.6733×10^{-1}	-25.104
B-35 (Control, Plot 2)	Constant	4.9761×10^{-1}	5.0448×10^{-1}	-20.519*
	Linear	6.2837×10^{-1}	6.4423×10^{-1}	-20.974
	Linear, 1st order Harmonic	6.1057×10^{-1}	6.3488×10^{-1}	-21.384
	Linear, Seasonal Factor	6.1057×10^{-1}	6.3488×10^{-1}	-21.384

*best model fit based on predictive log likelihood

CHAPTER 5: PHYTOREMEDIATION RESEARCH SUMMARY AND CONCLUSION

Wetlands have been impacted by the activities of man across the North American Continent. Industrialized areas that were once wetland habitats have been drained and put into other uses by landowners. The BASF Corporation site is no different. Having been a riparian wetland before the drainage and clearing by man, those wetland no longer function as a wetland. The release of anthropogenic chemicals into the soil and groundwater of these areas has provided options to restore the environment by phytoremediation using wetland species.

The use of emerging technology may often include techniques that are not necessarily proven before application and require study, as they become developed applications. Phytoremediation is such an emerging technology. Phytoremediation is a natural method that uses plants to detoxify organic and inorganic pollutants in groundwater and soil (Bollag et al., 1994). There are several potential phytoremediation mechanisms that can be encountered in part or whole within any application of phytoremediation technology. These include phytoextraction, rhizofiltration, phytostabilization, rhizodegradation, phytodegradation, and phytovolatilization (USEPA, 2000).

Phytoextraction is attributed to the removal of a contaminant by uptake processes into the plant tissue using translocation. Rhizofiltration and rhizodegradation both use the beneficial symbiotic relationships between soil microbes, plant roots, and exudates. Phytostablization can result in the fixation of mobile or toxic contaminants within the root zone either by immobilization through absorption and accumulation by roots, or precipitation within the soil in the root zone. Phytodegradation results when contaminants are degraded within plants through metabolic processes or through degradation external to the plant through the effects of enzymes produced by the plant.

Transformation, uptake and metabolism processes that occur within a particular application account for phytodegradation mechanisms. Uptake and transformation are dependent upon the contaminant hydrophobicity, solubility, and polarity. It has been generally assumed by many researchers that the octanol-water coefficient (K_{ow}) can provide a good indication of the degree of uptake that could be expected for a specific contaminant (Schnoor et al., 1995). Those contaminants found to have log K_{ow} values between 0.5 and 3 are most conducive to uptake in plants, while those with higher values may still be translocated into the plant, but will be less conducive to uptake mechanisms. Contaminants with high water solubilities and low sorption properties will also be more conducive to plant uptake. Hydrophobic compounds typically are found bound to the root surfaces or partitioned, but are not translocated beyond the roots (Schnoor et al., 1995). Nonpolar molecules with molecular weights less than 500 typically are found to adsorb to root surfaces. Conversely, polar molecules will enter the root and be translocated (Bell, 1992). Metabolism can play a significant role in the phytodegradation of contaminants as well. Herbicides such as atrazine are metabolized within the plant (Burken and Schnoor, 1997). Phytodegradation can result in the formation of toxic intermediate chemicals from the original contaminant or result in the creation of less toxic compounds, thus having a beneficial effect. Phytodegradation is a common process in hybrid poplar, black willow, and cypress trees (Shimp, 1993). Another related process that is sometimes found to occur with phytodegradation is phytovolatilization. It depends upon the same processes of metabolism, uptake and translocation that phytodegradation does, except that it results in the release of the metabolites or the contaminant itself into the atmosphere. It can often result in the production of less toxic compounds and can result in additional degradation through photodegradation.

Nineteen sites across the United States have been documented as applying phytoremediation techniques with willow tree species (USEPA, 2001). These sites include five that contain organic contamination and including one location that is attempting to phytoremediate a herbicide. Phytodegradation is suspected to be the leading mechanism involved at these phytoremediation sites.

In 1996, following the completion of a laboratory feasibility study, BASF Corporation (BASF) planted phytoremediation plots at a test location at its Geismar, Louisiana Facility. Two plots were planted with black willow (*Salix nigra*) to phytoremediate the herbicide bentazon from shallow groundwater. Plots of 1000 and 438 trees were planted spaced 2 meters apart in plots of 0.3 and 0.1 hectares, respectively. This test was undertaken as a response to the findings of a 1991 groundwater investigation to locate a new facility in an undeveloped area approximately 2 kilometers east of the Mississippi River. The target compound, bentazon, was manufactured by BASF until the late 1980's at Geismar. It is believed that after the storage of biosolids on the land surface in unlined impoundments, low concentrations of bentazon were released from the sludge into the shallow groundwater through rainfall. This was discovered in 1991. During the groundwater assessment of groundwater conditions, the geology, hydrology, soil chemistry and groundwater chemistry were characterized.

The test location is near the ancestral embayment of the Mississippi River and includes a thickening westward wedge of alternating alluvial silts, sands and clays. The upper zone is Holocene and rests on the lower erosional surface of the Pleistocene. Shallow groundwater is first encountered approximately 0.5 meters below ground surface in the Upper Zone. This zone is contaminated at the test site with bentazon, which was characterized at concentrations of between 1 to 10 mg/l in shallow groundwater.

Bentazon, a broad leaf, post-emergence herbicide is a non-polar, heterocyclic nitrogen compound that is moderately toxic. It is infinitely soluble in water and with a low log-octanol water coefficient and molecular weight. It does not easily biodegrade; however, it can be photodegraded and hydrolyzed within short periods of time. Its derivatives are formed by hydrolysis and are complexed by the addition of hydroxyl groups as they become more degraded and less toxic. The USEPA (1988) has placed a health advisory of 18 ug/l on drinking water to protect human health.

The BASF black willow phytoremediation study objectives were three fold: (1) estimate the water use of a black willow phytoremediation plot; (2) predict the probable length of time needed to adequately phytoremediate the site; and, (3) evaluate the effectiveness of the phytoremediation plots at reducing the contamination in shallow groundwater.

Water use of the tree plots was estimated during the 1998 and 1999 growing seasons, after 2 years of growth, using the tree-trunk heat balance method (Sakuratani, 1981; Baker and Van Bavel, 1987). Daily sap flow averaged 10 $l/day/m^2$ in Plot 1 and 6 $l/day/m^2$ in 1998 and 12 $l/day/m^2$ in both plots in 1999. These averages were standardized on a monthly basis and the annual water use was estimated at 3.6×10^6 for Plot 1 and

11.39 x 10^6 liters for Plot 2. Growth rates were measured by measuring the tree trunk thickness in 1998 and 1999 at the ground level. The test plot growth rates were measured and found to be 61% at Plot 1 and 57% at Plot 2 during 1998, and 40% at Plot 1 and 38% at Plot 2 during 1999. These growth rates and water use rates were used to complete the second study objective, to determine the length of time needed to phytoremediate the test site.

Groundwater models included the MODFLOW (McDonald and Harbaugh, 1988) and RT3D (Zheng, 1990) to determine the hydraulic flow simulation and the solute transport components of the test site. Correlations of the steady state potentiometric head and transient model potentiometric head were calibrated, and the accuracy determined by plotting the observed head against the modeled head for each observation point and plotting the best fit regression. Regression fitted trend lines suggested a better than 80% line fit to the actual data. Solute transport modeling predicted that the bentazon groundwater plume would most likely be at or below 18 ug/l after 22 years of phytoremediation at the test site. The groundwater model also predicted that plume migration would be controlled as well.

To accomplish the third objective, to determine the effectiveness of the phytoremediation plots, bentazon concentrations in groundwater monitoring well samples were studied to hypothesize possible effects and those hypotheses were tested with statistical analysis. Consideration was given to the Before After Control Impact (BACI) Model (Smith, 2002) to evaluate the data set. Fourteen monitoring wells were studied by preparing spatial isoconcentration maps of before-after data and by constructing line graphs of individual well sample data of the Before wells, the After wells, the Control wells. In summary, several hypotheses were made. First, both spatially mapped and graphically plotted data suggested that a decreasing trend existed in bentazon concentrations within both Plot 1 and Plot 2 between 1996 to 2001. Second, phytoremediation may be the direct cause for these trends since unaffected, control areas do not appear to indicate any change in bentazon concentrations from 1992 to 2001. To evaluate whether these observed trends were statistically significant, the BACI model required statistical testing. Two approaches to test the BACI model were used. First, an analysis of variance (ANOVA) model was used to test the significance of the decreases in the mean bentazon concentration in groundwater samples through time. Second, to evaluate any effect on bentazon concentration by other environmental factors and to further validate the ANOVA tests, Bayesian Time Series Analysis was used (Pole et al., 1994). Both statistics programs supported that bentazon concentrations were decreased from 1996 to 2001 at the test location and that phytoremediation is the most likely reason.

In conclustion, this research study is a comprehensive analysis of the phytoremediation of bentazon from before to after implementation. All research objectives were met. Water use of black willow in phytoremediation plots was successfully estimated and applied to a groundwater modeling of solute transport. This model enabled a prediction a 22-year time period to be necessary to completely reduce bentazon concentrations to below the groundwater health advisory level. This is one of the first successful groundwater modeling exercises of black willow phytoremediation. The black willow phytoremediation plots were statistically evaluated from groundwater samples collected from 1992 to 2001 in which evidence supports that phytoremediation accounted for decreases in bentazon concentration in shallow groundwater at the test location. This study is the first documented successful use of a BACI model to evaluate phytoremediation methods with black willow remediation of herbicides. This study has culminated as the successful development of scientific approaches to phytoremediation with black willow in the removal of the herbicide bentazon from shallow groundwater.

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VITA

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